REGIONAL AIR QUALITY: Photochemical Modeling for Policy Development and Regulatory Support

A Thesis
Presented to
The Academic Faculty

by

Michelle Silvagni Bergin

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the
School of Civil and Environmental Engineering

Georgia Institute of Technology
December 2006

REGIONAL AIR QUALITY: Photochemical Modeling for Policy Development and Regulatory Support

Approved by:

Dr. Armistead G. Russell, Advisor
School of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. M. Talat Odman
School of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. Alan J. Krupnick
Quality of the Environment Division
Resources for the Future

Dr. Ann Bostrom
School of Public Policy
Georgia Institute of Technology

Dr. James A. Mulholland
School of Civil and Environmental Engineering
Georgia Institute of Technology

Date Approved: November 8, 2006

Dedicated to Mike, Lucas, and Mia

ACKNOWLEDGEMENTS

I can't begin to adequately thank all the people that have supported me and who have shared this journey. In particular, the support, vision and guidance of Dr. Armistead Russell made this work possible, and I can not thank him enough for his patience and encouragement throughout the years. Additionally, I would like to thank Drs. Jhih-Shyang Shih and Alan Krupnick of Resources for the Future for their partnership and fortitude, and thank Dr. Krupnick for serving as a member of my Thesis Committee. Drs. M. Talat Odman, Jim Boylan, and Jim Wilkinson, greatly assisted in preparing and evaluating these modeling studies. Dr. Odman also provided the opportunity for my work on single-sources, along with Drs. Bill Chameides and Dan Cohan, and served as a member of my Thesis Committee. My other Thesis Committee members, Drs. Jim Mulholland and Ann Bostrom, provided valuable insights and discussion. I have also benefited from collaboration with Drs. Terry Keating, Jason West, and Amir Hakami, who added new perspectives throughout our work together. Dr. Yongtao Hu and Didier Contis provided much needed and appreciated system support. And, of course, my fellow graduate students in the Russell Group and in Environmental Engineering were great companions along the way. The GA Tech community has provided a wonderful learning experience and I am grateful to have had the opportunity to study here. Finally, I would like to thank my husband Mike for all his incredible support and for sharing so much of this experience. Our children Lucas and Mia created an entire new dimension to these years, and I would like to thank them just for being here, and our families for being as much a part of this as possible, despite the distances.

This work was made possible through funding support by the EPA/NCER STAR Graduate Fellowship program, a Georgia Institute of Technology Presidential Fellowship, and an EPA/NSF Partnership Grant. Partial funding was also provided under US EPA grants RD82897602, RD83107601, and RD83096001, and the U.S. Department of Justice in support of Civil Action No. C2-99-1181.

TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS iv

LIST OF TABLES xi

LIST OF FIGURES xii

SUMMARY xvii

CHAPTERS

1 INTRODUCTION 1

1.1 Air Quality and its Regulation in the United States 1

1.2 Regional Pollutants and Their Control 4

1.3 Air Quality Models 9

1.4 Structure and Scope of this Thesis 11

1.4.1 The URM-1ATM Air Quality Model 12

1.4.2 Chapter Descriptions 14

References 18

2 REGIONAL AIR QUALITY: Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States 23

Abstract 23

2.1 Introduction 24

2.2 Method 26

2.2.1 Modeling Domain and Episodes 26

2.2.2 Model Description and Data Inputs 30

2.3 Results 31

2.3.1 Model Performance Evaluation 31

2.3.2 2010 Simulated Pollutant Concentrations and Sensitivities 33

2.3.2.1 Source-Receptor Coefficient (SRC) and Impact Factor (IF) Calculations 37

2.3.2.2 Comparison of Episode and Emissions Category Contributions 39

2.3.2.3 States as Sources 40

2.3.2.4 States as Receptors 44

2.4 Discussion 48

Acknowledgments 49

References 51

3 SINGLE-SOURCE IMPACT ANALYSIS USING 3D AIR QUALITY MODELS 56

Implications 56

Abstract 56

3.1 Introduction 57

3.1.1 Ozone Chemistry and Power Plant Plumes 61

3.2 Method 63

3.2.1 Models and Input Data 63

3.2.2 Sensitivity Analysis 66

3.3 Results 68

3.4 Conclusions 74

Acknowledgments 75

References 76

4 VOLATILE ORGANIC COMPOUNDS AND COOPERATIVE POLICY DEVELOPMENT AND SUPPORT 81

4.1 Introduction 81

4.2 Organic Solvent Impacts on Tropospheric Air Pollution 83

4.2.1 Sources and Impacts of Volatile Solvents 83

4.2.2 Modes and Scales of Impact 85

4.2.2.1 Direct Exposure 86

4.2.2.2 Formation of Secondary Compounds 87

4.2.2.3 Spatial Scales of Secondary Effects 87

4.2.2.3.1 Global Impacts 88

4.2.2.3.2 Stratospheric Ozone Depletion 89

4.2.2.3.3 Global Climate Forcing 90

4.2.2.3.4 Urban and Regional Scales 91

4.2.3 Tropospheric Ozone 91

4.2.3.1 Effects 92

4.2.3.2 Tropospheric Photochemistry and Ozone Formation 93

4.2.3.3 Assessing Solvent Impacts on Ozone and VOC Reactivity 96

4.2.3.3.1 Quantification of Solvent Emissions on Ozone Formation 98

4.2.3.3.2 Experimental Analysis 98

4.2.3.3.3 Computational Analysis (Air Quality Models) 99

4.2.4 Regulatory Approaches to Ozone Control and Solvents 102

4.2.5 Summary 103

References 105

4.3 The Development and Expansion of Regulatory Applications Accounting for the Ozone Formation Potentials of Volatile Organic Compounds 109

4.3.1 History of Ozone Management 109

4.3.2 Barriers to Accounting for Reactivity in Regulatory Application 110

4.3.2.1 Quantification of Reactivity 111

4.3.2.2 Uncertainty 113

4.3.2.3 Variability 114

4.3.3 Regulatory Applications and Future Potential Applications 115

4.3.3.1 Alternative Fuel Reactivity Adjustment Factors 115

4.3.3.2 Aerosol Coatings 116

4.3.3.3 Industrial Stack Emissions 117

4.3.3.4 Extension of Reactivity Weighting Applications 118

4.3.3.4.1 EPA Support for Reactivity Accounting in SIPs 118

4.3.3.4.2 Collaborative Efforts for Regional and National Applications 118

4.3.3.4.3 Regional Modeling of Reactivity 119

4.3.4 Conclusions 119

References 121

5 REGIONAL ATMOSPHERIC POLLUTION AND TRANSBOUNDARY AIR QUALITY MANAGEMENT 126

Abstract 126

5.1 Regional Air Pollution 127

5.2 General Characteristics of Regional Atmospheric Transport and Chemistry 129

5.3 Regional Air Pollutants and Effects 132

5.3.1 Acid Deposition 133

5.3.2 Tropospheric Ozone 138

5.3.3 Particulate Matter 143

5.3.4 Mercury 149

5.3.5 Persistent Organic Pollutants 154

5.3.6 Regional Climate Change 157

5.3.6 A Unified View 158

5.4 Management of Regional Transboundary Air Pollution 159

5.4.1 Examples of Transboundary Air Quality Management Regimes and Approaches 162

5.4.1.1 Emission Trading of SO_2 for Acid Deposition Control 162

5.4.1.2 Regional NO_x Control for Ozone in the United States 163

5.4.1.3. Cooperative Air Pollution Control in Europe 164

5.5 Achieving Successful Regimes for Transboundary Air Pollution 165

5.6 Assessment of Existing International Regional Regimes 168

5.6.1 Europe 168

5.6.2 North America 169

5.6.3 Asia 170

5.7 Regimes to Address Pollutant Transport Beyond the Regional Scale 171

5.8 Summary and Conclusions 173

Acknowledgments 175

References 177

6 CONCLUSIONS AND FUTURE RESEARCH 191

6.1 Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States 191

6.2 Single-Source Impact Analysis Using 3D Air Quality Models 192

6.3 Impacts of Volatile Organic Compounds on Air Quality and the Development and Expansion of Regulatory Applications Accounting for their Ozone Formation Potentials 194

6.4 Regional Atmospheric Pollution and Transboundary Air Quality Management 195

APPENDIX A: Supplemental Information to Chapter 2. 198

APPENDIX B: REACTIVITY ASSESSMENTS:
A Report to the Relative Reactivity Working Group 230

APPENDIX C: Ozone formation potential of organic compounds in the eastern United States: A comparison of episodes, inventories, and domains (Hakami, A., M.S. Bergin, and A.G. Russell, 2004. *Environmental Science & Technology*, **33**(24), 6748-6759.) 276

LIST OF TABLES

		Page
Table 3.1:	NO_x emissions estimated by the Court to have been released from the Sammis power plant (tons/month).	64
Table 3.2:	Sum of model cell hourly maximum increases and decreases in ozone concentration accounting for first and second order sensitivity response to excess NO_x emissions from the Sammis plant.	73
Table 4.1:	Percentage of ozone production attributable to each organic. [Adapted from F.M. Bowman and J.H. Seinfeld, J Geophys. Res., 99, 5309, (1994), and M.S. Bergin et al., *Env. Sci. Technol.*, 29, 3029 (1998)]	97
Table A.1:	Mean Normalized Bias and Mean Normalized Error of ozone predictions (%).	207
Table A.2:	Mean Fractional Bias and Mean Fractional Error of $PM_{2.5}$ and sulfate predictions (%).	208
Table B.1:	Summary of compound reactivity modeling studies.	264
Table B.2:	Summary of major characteristics of Carter (1994) reactivity scales.	265
Table B.3:	Summary of source emissions reactivity modeling studies	266
Table B.4:	Regression results for airshed model exposure vs. MIR and airshed peak ozone vs. MOIR measures (Bergin et al., 1996, 1998).	267
Table B.5:	Normalized bias and standard deviation between reactivity metrics calculated using the CIT-S90 airshed model (Bergin et al., 1996, 1998).	267
Table B.6:	Example MIRs and variations between locations (mean and standard deviation) (Russell et al., 1995).	267
Table B.7:	Comparision of relative reactivities calculated using the SAPRC90 and the Carbon Bond 4 mechanisms.	268
Table B.8:	Effect of SAPRC mechanism updates on calculated MIR's.	
Table B.9:	Rank ordering and source attribution of uncertainty in relative reactivities for airshed modeling of Los Angeles.	269

LIST OF FIGURES

Page

Figure 1.1: Schematic of the unified chemistry of regional ozone, particulate matter, acids, and mercury. 7

Figure 1.2: Ozone isopleth diagram of lines of constant concentration showing the dependencies of ozone on varying levels of initial VOCs and NO_x. (Bergin and Russell, 2001). 8

Figure 1.3: Multiscale simulation grid designed for regional control strategy evaluations. . 13

Figure 2.1: Multiscale modeling grid. 27

Figure 2.2: Average daily emissions of elevated NO_x, surface NO_x, and total SO_2 per state (tons/day), projected to the year 2010. 29

Figure 2.3: (a) Eight-hour averaged ozone concentration and its sensitivity to a 30% reduction in (b) domain-wide NO_x emissions, and (c) in surface NO_x emissions from Virginia and (d) from Tennessee, and in (e) elevated NO_x emissions from Virginia and (f) from Tennessee. 34

Figure 2.4: (a) Twenty-four hour averaged $PM_{2.5}$ concentration and (b) its sensitivity to 30% reductions in SO_2 , surface NO_x, and elevated NO_x emissions domain-wide, (c) reductions from Virginia, and (d) reductions from Tennessee 35

Figure 2.5: Comparison of average contributions from source states to ozone and $PM_{2.5}$ Source Receptor Coefficients for each episode and emissions category. 40

Figure 2.6: Ozone (a) Source Receptor Coefficient contributions from one ton reductions in surface NO_x emissions during the July episode, and (b) Source Receptor Impact Factor contributions from 30% reductions in surface and elevated NO_x emissions during the July episode. 41

Figure 2.7: $PM_{2.5}$ (a) Source Receptor Coefficient contributions from one ton reductions of SO_2 averaged over the July, May, and February episodes, and (b) Source Receptor Impact Factor contributions from 30% reductions in SO_2, surface, and elevated NO_x emissions averaged over the July, May, and February episodes. 42

Figure 2.8: Comparison of spatial and population-weighted Source Receptor Impact Factors in each receptor state from local and regional sources for (a) 8-hour ozone sensitivity to 30% reductions in surface and elevated NO_x emissions combined during the July episode, and (b) daily $PM_{2.5}$ sensitivity to 30% reductions in SO_2 and surface and elevated NO_x emissions, averaged over the July, May, and February episodes. 45

Figure 2.9: Source Receptor Impact Factors in each state for (a) ozone sensitivity to 30% reductions in surface and elevated NO_x emissions during the July episode, and for (b) $PM_{2.5}$ sensitivity to 30% reductions in SO_2, surface, and elevated NO_x emissions averaged over the July, May, and February episodes. 47

Figure 3.1: Model grids used for (a) URM-1ATM, with the location of the Sammis power plant, and (b) CMAQ simulations. 60

Figure 3.2: Comparison of the maximum increase in hourly-averaged ozone concentrations due to excess NO_x emissions from the Sammis plant calculated using DDM with the URM model during the periods of (a) July 11-19, 1995 and (b) May 24-29, 1995, and using (c) the CMAQ model during August 12-20, 2000. 69

Figure 3.3: Brute-force estimates of maximum increase in hourly-averaged ozone concentrations due to excess NO_x emissions from the Sammis plant using (a) the URM model applied to the July episode and (b) the CMAQ model applied to the August episode. 70

Figure 3.4: Maximum increases in hourly-averaged ozone concentrations due to a 10% increase of NO_x emissions from the Sammis plant during the July 11-19, 1995 period: (a) from its actual location collocated with the Cardinal power plant and (b) from one cell to the north. 71

Figure 3.5: Maximum decreases in hourly-averaged ozone concentrations due to excess emissions from the Sammis power plant during the August episode. 72

Figure 3.6: Maximum (a) increases and (b) decreases in hourly-averaged ozone concentrations per model cell due to excess emissions from the Sammis power plant during the August episode when ozone concentrations are greater than 0.060 ppm. 73

Figure 4.1: Ozone isopleth diagram of constant concentration showing the dependencies of ozone on varying levels of initial VOCs and NO_x. 95

Figure 4.2: Solvent relative reactivities based on mass of ozone formed per gram of solvent emitted into the gas phase. [Adapted from M.S. Bergin et al., (1998) and M. Khan et al., (1999)] 102

Figure 4.3: Comparison of MIR 1-hour average ozone reactivity metrics for each episode calculated using the URM-1ATM with DDM-3D, and comparison with the corresponding Carter MIR values. 113

Figure 5.1: Observed values of volume-weighted annual average pH of precipitation. Reproduced with permission from (Rodhe et al., 2002). 134

Figure 5.2: NO_x from anthropogenic sources in 1995. Reproduced with permission from (RIVM, 1995). 136

Figure 5.3: SO_2 from anthropogenic sources in 1995. Reproduced with permission from (RIVM, 1995). 136

Figure 5.4: Schematic of the unified chemistry of regional ozone, particulate matter, acids, and mercury. 137

Figure 5.5: Regional ozone and sensitivity to emissions. (a) Simulated one-hour averaged ozone concentration and (b) its sensitivity to a 30% reduction in surface NO_x emissions from Tennessee (Bergin et al., 2006a). 141

Figure 5.6: Satellite image from the Earth Probe Total Ozone Mapping Spectrometer of smoke/dust (absorbing aerosols) over North America on May 15, 1998 (EPA, 2003). Image developed by the Earth Observatory team, GSFC/916, and reproduced with permission. 148

Figure 5.7: Regional particulate matter and its sensitivity to emissions. (a) Simulated 24-hour averaged $PM_{2.5}$ concentration and (b) its sensitivity to a 30% reduction in SO2 emissions from Tennessee (Bergin et al., 2006a). 149

Figure 5.8: Conceptual biogeochemical mercury cycle. Reproduced with permission from (EnvCan, 2004). 151

Figure 5.9: Estimated global emissions of mercury in 1995. Reproduced with permission from (Pacyna et al., 2003). 153

Figure 5.10: Modeled benzo[a]pyrene (BaP, a PAH) depositions from emissions in France in 2001, g/km2/year. Reproduced with permission from (EMEP, 2004). 156

Figure A.1: Measured, reconstructed, and modeled $PM_{2.5}$ concentrations in (a) July and (b) May from the IMPROVE sites and (c) on July 14 from the Cass sites. 209

Figure A.2: Measured and modeled sulfate concentrations in (a) July and (b) May from the IMPROVE sites and (c) on July 14 from the Cass sites. 211

Figure A.3: Ozone Source Receptor Coefficient contributions from one ton reductions in (a) elevated NO_x emissions during the July episode and (b) surface NO_x and (c) elevated NO_x emissions during the May episode 214

Figure A.4: $PM_{2.5}$ Source Receptor Coefficient contributions from one ton reductions of (a) surface NO_x and (b) elevated NO_x averaged over the July, May, and February episodes. 216

Figure A.5: Comparison of spatial and population-weighted Source Receptor Impact Factors contributed by each state to local and regional (a) ozone from surface and elevated NO_x emissions for the July episode and (b) the May episode, and (c) to $PM_{2.5}$ from SO_2 and surface and elevated NO_x emissions averaged over the July, May, and February episodes. 217

Figure A.6: Comparison of spatial and population-weighted Source Receptor Impact Factors on ozone in each receptor state from local and regional surface and elevated NO_x emissions for the May episode. 219

Figure A.7:Source Receptor Impact Factors in each state for ozone sensitivity to 30% reductions in (a) surface NO_x and (b) to elevated NO_x emissions during the July episode, and (c) to surface NO_x and (d) to elevated NO_x emissions during the May episode. 220

Figure A.8: Ozone Source Receptor Coefficients in receptor states from one ton reductions in (a) surface NO_x and (b) from elevated NO_x emissions during the July episode, and (c) from surface NO_x and (d) from elevated NO_x emissions during the May episode. 223

FigureA.9: $PM_{2.5}$ Source Receptor Coefficients in receptor states from one ton reductions of (a) SO_2, (b) surface NO_x, and (c) elevated NO_x emissions averaged over the July, May, and February episodes. 225

Figure B.1: Dependence of peak ozone and $d[O_3]/d[VOC]$ on VOC and NO_x. 271

Figure B.2: Comparison of MIR, MOIR, and POCP relative reactivities. 272

Figure B.3: Relative (normalized) N-MIR and N_MOIR reactivities for six solvents (Kahn et al., 1997). 272

Figure B.4: Box plots of the calculated (a) net reactivities (NRs) and (b) normalized reactivities (RAFs) across cities (Russell et al., 1995). 273

Figure B.5: Comparison of three-dimensional and trajectory modeled relative reactivities. 273

Figure B.6: Spatial distribution of relative reactivities (Yang et al., 1999). 274

Figure B.7: Mean values and 1s uncertainties of MIRs for selected organic compounds, calculated with the SAPRC90 and SAPRC97 mechanisms. 275

Figure B.8: Spatial exposure normalized reactivity predictions from rate constant uncertainty adjustments (Bergin et al., 1998). 275

SUMMARY

One of the more frustrating air quality challenges is the control of tropospheric ozone, which is responsible for widespread and serious impacts on human health. Research also now implicates ambient particulate matter with aerodynamic diameters of 2.5 microns and less ($PM_{2.5}$) as contributing to extensive damage to human health, and current scientific understanding suggests that these concentrations will also be difficult to manage. In addition to human health, both of these pollutants also impact the environment and regional and global climate systems.

In the United States, emissions contributing to ozone and particulate matter have been regulated since the early 1970s. More than thirty years later, over half of the population in the United States still experiences exposures to concentrations of pollutants, largely ozone and $PM_{2.5}$, exceeding the NAAQS. An important factor contributing to the lack of success in controlling these pollutants is that while the standards for these pollutants are set at the federal level, the responsibility for achieving the standards is largely delegated to individual states. As a result, emissions control and impact analysis have largely been performed at the urban scale, while both of these pollutants have large regional components, with emissions impacting concentrations 100s to 1000s of kilometers away.

Because of the complexity of responses in the atmospheric system, potential air quality control strategies are generally evaluated with the use of predictive computational models. Recent advancements in numerical techniques and in representation of aerosol chemistry and dynamics in an Eulerian, photochemical grid model have facilitated three novel evaluations of emissions impacts on regional scale ozone and $PM_{2.5}$, which are presented in this thesis. To perform these evaluations, a multiscale grid was designed to follow pollutant transport and transformation in the eastern half of the United States, emphasizing areas with large emission sources and high population densities. Emissions

and meteorological data were prepared for three seasonal episodes occurring in February, May, and July.

The first modeling application is an evaluation of local and interstate impacts on ozone and $PM_{2.5}$ from ground-level and elevated NO_x and SO_2 emissions from individual states. This analysis identifies states responsible for a significant amount of regional secondary pollution, and states which do not have independent control over much of their pollution concentrations. An average of approximately 77% of each state's ozone and $PM_{2.5}$ concentrations that are sensitive to the emissions evaluated are found to be due to emissions from other states rather than to local emissions.

The second application is an assessment of impacts from emissions from a single power-plant on resulting regional ozone concentrations. This application is the first to utilize advanced sensitivity techniques in 3D, regional photochemical models for evaluation of single-source emissions impacts, and two air quality models and three sensitivity techniques are applied. Ozone increases greater than 0.5 ppbv occurred over eight states downwind from the power-plant. This study was performed in support of a recent compliance enforcement action to assess the extent of ozone formed from approximately 2500 excess tons of NO_x emissions per month above the permitted rate from a power-plant in Ohio, resulting in a settlement in excess of $1.1 billion.

The third application presented is part of a body of research aimed at advancing understanding of the ozone formation potential, or 'reactivity', of VOCs for use in regulatory applications. In this chapter, the total air quality impacts of VOCs emissions from solvent use and manufacture (one of the dominant sources of anthropogenic VOCs) are addressed, including effects on tropospheric ozone formation. Then, research addressing scientific barriers to accounting for reactivity in regulations is reviewed, resulting current and upcoming regulatory applications are described, and results from a modeling extension of reactivity quantification to the regional scale are presented. An important feature of this research program has been the collaborative and iterative

process of regulatory development, combining participation from scientific, regulatory, and regulated communities.

These three applications together provide powerful approaches for integrating air quality evaluation and management across regulatory boundaries in the United States. This thesis concludes with a broad evaluation of regional atmospheric pollution and transboundary air quality management, including international efforts, and an analysis of successful transboundary management approaches, emphasizing the need for integrated control strategies addressing different pollutants, emissions sources, and spatial scales, accounting for their tightly linked physical and chemical systems.

CHAPTER 1

INTRODUCTION

1.1 Air Quality and Its Regulation in the United States

Short- and long-term effects of anthropogenic emissions to the atmosphere are varied, including acid deposition, climate change, the depletion of stratospheric ozone, bioaccumulating organics and metals, and urban, regional, and global air pollution (CARB and ALA, 2004; EPA, 2006a). Air pollution poses a direct significant risk to human health, and current levels of regulated pollutants in the United States are associated with increases in premature deaths, hospital admissions, and emergency room visits, and lead to restricted activity levels (Brunekreef and Holgate, 2002; Frumkin, 2002). In California, the number of premature deaths linked to particulate matter (PM) alone is estimated at more than double the number of deaths caused by traffic accidents, shortening lives by an estimated average of 14 years (CARB and ALA, 2004). Research on populations in other countries find similar results (Frumkin, 2002), and studies also find further damaging health effects from ozone, airborne metals, and toxic and persistent organic compounds [(Bergin *et al.*, 2005) and references therein].

While city-level air pollution regulations have existed in the United States since at least 1881, the Air Pollution Control Act of 1955 was the nation's first federal air quality legislation, which evolved into the Clean Air Act (CAA) of 1963. In 1970, major amendments to the CAA and the National Environmental Policy Act were passed, and the Environmental Protection Agency was created, framing the air quality regulatory structure existing in the United States today. Of particular importance, the 1970 CAAA established National Ambient Air Quality Standards (NAAQS), which were amended to their current form in 1990 (Lewis, 1985; Percival *et al.*, 1996; AMS, 1999). The NAAQS identifies criteria pollutants and sets maximum allowable outdoor levels for each to

protect public health (the primary standards) and public welfare (the secondary standards).

In 2002, over half of the population in the United States lived where monitored air pollution exceeded the NAAQS, the majority of which was due to ozone and particulate exposure (Census, 2002; EPA, 2002c). Still, the benefits of reduction in the six criteria pollutants addressed by the NAAQS have been substantial, including an estimated 100,000 to 300,000 fewer premature deaths and 30,000 to 60,000 fewer children born with IQs below 70 (EPA, 1997a). Economic benefits associated with avoided health impacts are estimated to be $400 billion (1997 USD) for the year 2000, although $250 billion in costs are associated with remaining uncontrolled air pollution (Yang *et al.*, 2005). The same study estimates a total benefit from these regulations of $7.9 trillion (2000 USD) for the period of 1970-2000, in comparison with an estimated benefit of $27.6 trillion (2000 USD) by the US EPA for the same period (Yang *et al.*, 2005). In these estimates, ozone and PM are by far the largest sources of damage/benefit. In comparison, the EPA estimated the direct costs of implementing the Clean Air Act from 1970 to 1990 to total $523 billion (1990 USD) (EPA, 1997a). In addition to the costs associated with heath effects, air pollution also impacts the economy by damaging materials and historic monuments and reducing crop and timber yields, accounting for an estimated several billion dollar loss every year in the United States from crop damage alone (Tingey *et al.*, 1994).

Since 1970, some air quality control efforts have had great success, such as the reduction of lead and SO_2, and some have been frustrating, such as the control of ozone and particulate matter. A National Research Council report published in 1991 (NRC, 1991) stated that "[d]espite more than two decades of massive and costly efforts to bring this problem under control, the lack of ozone abatement progress in many areas of the country has been disappointing and perplexing." While many areas now have lower levels of ozone than previous years, the lead finding of the NRC report was that "…

efforts to attain the National Ambient Air Quality Standard for ozone largely have failed." A subsequent NRC report in 2004 speculates that "[t]he complex O_3-formation process, which involves the interaction of NO_x, VOCs, and dynamic atmospheric processes, has probably contributed to the difficulties encountered in abating O_3 pollution in the United States." (NRC, 2004) The first two decades of O_3 control efforts focused on VOC reduction, and the need for substantial NO_x reductions was not understood until the late 1980s when major deficiencies in the emission inventories were identified (NRC, 2004). Further progress in ozone management is being gained by the application of reactivity-based reduction rather than mass-based reduction of VOC emissions, as discussed further below.

Control of particulate matter has proven difficult for other reasons. While both ozone and PM were designated as criteria pollutants in the original 1970 NAAQS (ozone as a photochemical oxidant), PM was first regulated as Total Suspended Particulate, defined as particles measured with aerodynamic diameters less than approximately 24-45 μm. In 1987, the NAAQS was revised to control PM with aerodynamic diameters of 10 μm or less (PM_{10}), and, in 1997, was further revised to independently address coarse (PM_{10}) and fine particles, those with aerodynamic diameters of 2.5 μm or less ($PM_{2.5}$). Industries and regulators often need to develop and implement new control measures after each NAAQS revision. This evolving standard, while difficult to meet, reflects an increasing ability to measure and monitor dynamic ambient concentrations and therefore identify associated health and environmental outcomes. Particles in different size ranges have different modes of emission and/or formation and removal, as well as different sources and impacts. Despite substantial reductions in PM, our success in controlling it is disappointing considering that we have attempted to address the problem for over three decades yet health and environmental impacts remain significant.

While the reasons for the lack of response of ozone and PM to controls differ, a common characteristic of ozone and a large component of $PM_{2.5}$ is that they are

secondary in origin, meaning they are formed in the atmosphere rather than being emitted directly. Sources of precursor emissions contributing to secondary pollutants may be extremely pervasive (such as NO_x which contributes to both ozone and particulate matter), difficult and/or expensive to reduce, difficult to identify (such as for the organic component of particulate matter), or highly variable (such as emissions from biogenic sources).

Another contributing factor to our difficulty in controlling these pollutants is that while the U.S. EPA establishes the NAAQS, each state is largely delegated the responsibility to figure out how to achieve them (Percival *et al.*, 1996). Some programs and provisions allow states to address interstate transport of air pollutants, but historically the U.S. air quality control regulatory system treats most air quality issues in each state relatively independently by requiring State Implementation Plans (SIPs) for states out of attainment with the NAAQS. Some federal standards are specified for specific sources such as motor vehicles and major new stationary sources, and through a SIP each state further controls emissions within its borders in an attempt to hold ambient pollutant concentrations below the federal standards. However, secondary pollutants can be strongly dependent on emissions from upwind states. If a large fraction of these pollutants are caused by out-of-state emissions, then statewide plans alone may fail and regional actions must be designed and adopted. Even if a state could meet the NAAQS alone, stakeholders in that state may be required to invest a level of resources that could be more effectively applied by reducing emissions located in other states.

1.2 Regional Pollutants and Their Control

Both the scientific and political communities now increasingly recognize that several important air pollutants, including ozone, particulate matter, mercury, acids, and persistent organic pollutants (POPs), are regional in nature. These pollutants and/or their precursors can be transported over scales from about 100 to a few 1000s of kilometers,

large enough to cross state, provincial, national, and continental boundaries. Managing these pollutants cooperatively can require overcoming political, economic, and cultural differences, and requires recognition of the complex linkages between pollutants, emissions, and short- and long-term impacts (Bergin *et al.*, 2005). Further, a number of significant pollutants share common sources, and actions to reduce one pollutant may exacerbate concentrations of another. Efficient management must account for the linkages between affected pollutants.

Some programs are being or have been developed to manage regional pollution in the United States, such as SO_2 emissions trading for electric utilities and the NO_x SIP call (also called the NO_x Budget Trading Program), and, more recently, the Clean Air Interstate Rule and the Clean Air Mercury Rule. Some mechanisms are also available to states under the CAAA to challenge interstate transport of pollutants, however other than actions addressing the control of acid rain, these provisions have been largely ineffective (Percival *et al.*, 1996). A Subcommittee under the Federal Advisory Committee Act was established in 1995 incorporating a broad group of stakeholders to provide advice to the U.S. EPA regarding integrated, regional approaches to attaining the NAAQS and reducing regional haze. This Subcommittee developed and endorsed a guiding set of nine "Content-Related Principals" to aid in the design of a regional approach to air quality management (FACA, 1998). In addition, the 2004 National Research Council report concludes that structural changes are needed to the U.S. regulatory system in order to address the regional component of air pollution (NRC, 2004).

To develop effective regional policy and to support regulatory implementation, reliable information characterizing interstate air pollution must be available to federal- and state-level decision makers, enabling states to both identify external emissions impacting their in-state pollution and to understand the extent to which other states are affected by their emissions so they can participate in cooperative mitigation efforts. As our understanding and characterization of regional air pollution contributions and impacts

increases, air quality management has a greater opportunity to more effectively control it through programs such as emissions trading and collaborative regional planning, more effective compliance enforcement, and more specific development planning such as for a new source location or existing source expansion. Recent control efforts have been very successful when states have had options and flexibility in designing strategies that also support priorities and goals other than air quality, such as growth and economic vitality, rather than having imposed 'command and control' requirements. However, as illustrated by early levels of urban air pollution here and in other countries, federal standards and oversight are necessary to ensure a minimum level of protection for human health and the environment. In addition to enabling interstate cooperation, strong scientific understanding of regional air pollution is also needed to support joint efforts to control pollutants that cross shared international borders, and is a critical step towards broader international efforts in the mitigation of increasingly significant levels of long-range and globally transported air pollutants (IPCC, 2001; Fiore *et al.*, 2002c; Bergin *et al.*, 2005).

In general, outdoor air pollution largely results from combustion of fossil fuels for transportation, power, and other human activities (WHO, 2004) and from biomass burning, although natural sources and ambient meteorological conditions play important roles in determining the ultimate impact of those anthropogenic emissions. Precursors to secondary air pollution, notably NO_x, SO_2, and VOCs, are emitted at different rates and with differing spatial and temporal patterns, and may be dependant on properties such as temperature, humidity, and cloud cover. Pollutants are removed by chemical reactions, transport, and wet and/or dry deposition, all of which depend on meteorology (i.e. wind speed, rain) and on what surfaces are available (i.e. buildings, grasses, trees). Finally, the coupled chemical reactions that drive secondary pollutant formation are also dependant on many dynamic variables, including meteorology and chemical composition of the surrounding atmosphere.

Ozone is a classic example for illustrating the complexity of secondary pollutant formation. Tropospheric ozone production involves reactions between volatile organic compounds (VOCs) and NO_x in the presence of sunlight (Figure 1.1). NO_x is emitted by many combustion sources, such as automobiles, trucks, and industrial plants. VOCs are composed of hundreds of differing species with differing sources of emissions (e.g. biogenics, automobiles, solvents, restaurants) and of potential chemical reactions. Other pollutants, for example PM and acids, compete for some precursor species (Figure 1.1).

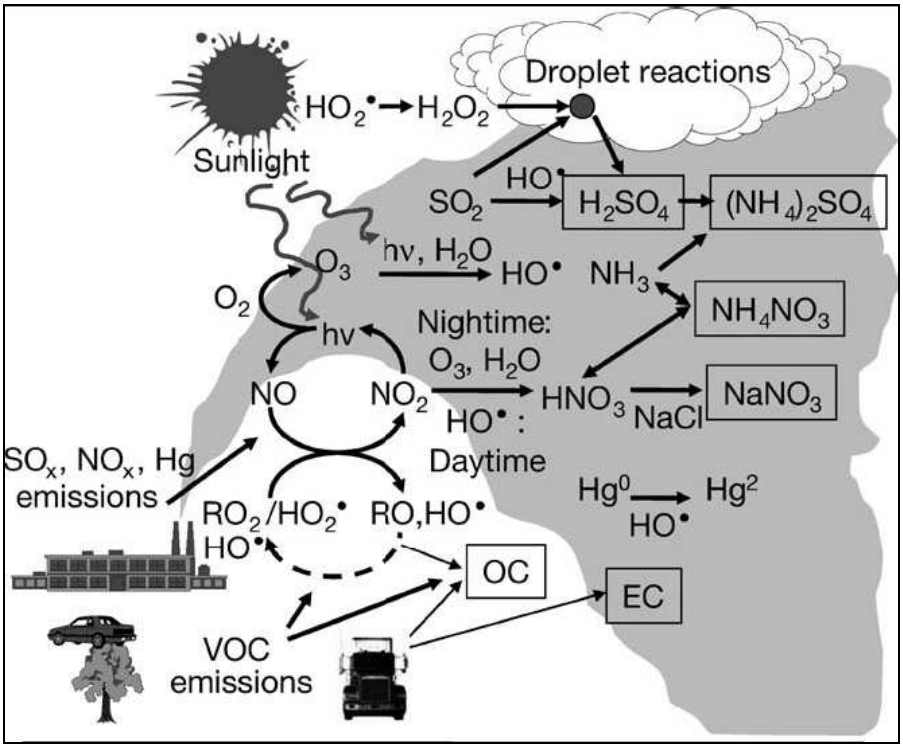


Figure 1.1 Schematic of the unified chemistry of regional ozone, particulate matter, acids, and mercury. Particulate phase species are boxed.

The production of ozone from NO_x and VOCs is not straight forward. While NO_x availability ultimately limits ozone production, the amount and rate of production is dependant on the local VOC to NO_x ratio (e.g. Figure 1.2). Under certain polluted, VOC-

limited conditions (i.e. low VOC to NO_x ratios) and at night, ozone concentrations increase with reductions in NO_x emissions. Under VOC-limited conditions ozone concentrations decrease with VOC reduction, although to varying degrees depending on the VOC and other factors. Therefore, VOC reduction can be a complimentary strategy to NO_x reduction for many highly polluted areas. Some airsheds may also have unique chemical compounds present that interact within this cycle, such as has been hypothesized if high levels of chlorine exist (Knipping and Dabdub, 2003; Tanaka *et al.*, 2003; Chang and Allen, 2006). Finally, ozone production may be delayed by the formation of organonitrates, such as PAN and PPN. These compounds are formed from NO_x and may be transported long distances before decomposing, releasing NO_x to produce ozone far from the original sources.

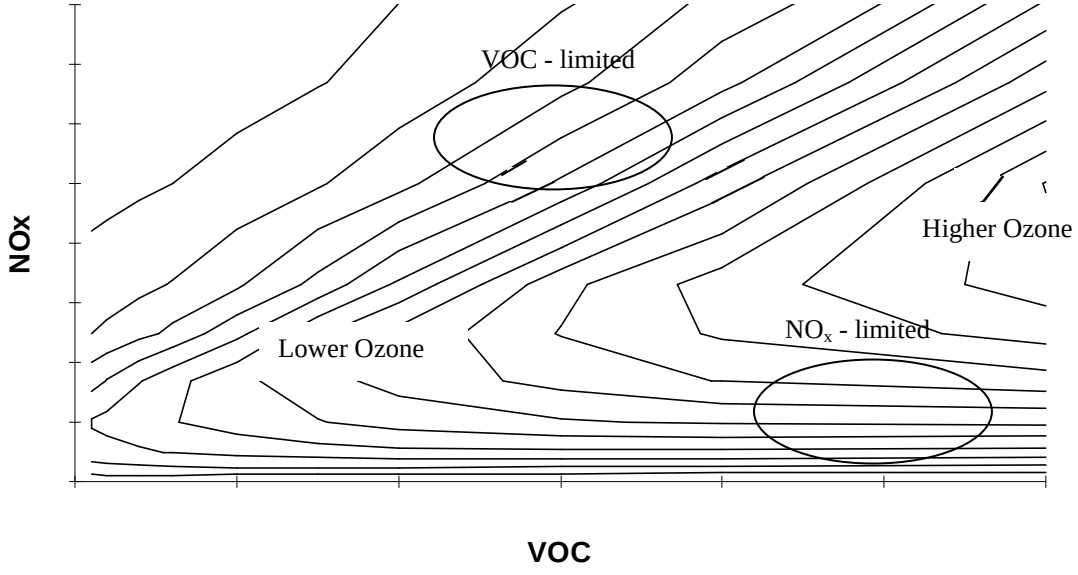


Figure 1.2 Ozone isopleth diagram of lines of constant concentration showing the dependencies of ozone on varying levels of initial VOCs and NO_x. The shape of the isopleths varies with location. Concentrations are given in ppb (Bergin and Russell, 2001).

Because of these complex interactions, it is difficult to design effective pollution control strategies; however, because implementing emissions reductions can be expensive, potential impacts must be as fully assessed as possible before any are selected. In addition to wasting valuable resources, if regulations for emissions reductions are unsuccessful, then future strategies for pollution control may be met with distrust and resistance. Policy design requires a broad range of tools for the analysis and comparison of the potential outcomes of various control options before regulations are imposed.

1.3 Air Quality Models

A powerful tool available to policy decision makers for the detailed evaluation of potential control strategies is the use of air quality models (AQMs) (Russell and Dennis, 2000; NRC, 2004). AQMs are computerized representations of the processes responsible for air pollution. AQMs exist as single-cell ('box') models, Lagrangian ('trajectory') models, and Eulerian ('grid') models. These models mathematically simulate the atmosphere in varying degree of detail by representing emissions; initial and boundary concentrations of chemical species; the chemical reactions of the emitted species and of their products; and meteorology such as solar radiation, wind, and temperature. Grid models represent great physical detail and are able to account for nonlinearities in atmospheric processes which become important under conditions such as those encountered during long-range transport, multi-day periods, and high concentration episodes. These models provide spatial and temporal information on pollutant behavior for specific pollution scenarios and are typically used in regulatory or policy assessments to simulate impacts from source categories over large spatial scales (EPA, 2006b). Single-cell models are used to represent a wide variety of detailed chemical conditions and to perform formal sensitivity analysis. Trajectory models can also be used for formal analysis of uncertainty [e.g. (Bergin *et al.*, 1999b; Bergin and Milford, 2000)] or to span results between box and gird models, for example reducing a set of uncertain parameters

identified with box models for the analysis of uncertainty using a grid model (Yang *et al.*, 1995; Bergin *et al.*, 1998a).

Models enable us to combine our understanding of the atmosphere's chemistry and meteorology with estimates of source emissions and physical parameters to predict effects of emissions reduction on pollutant formation, transport, and deposition. AQMs also aid in identifying gaps in data, chemical reaction representation, or other processes. These models are essential in evaluating control strategies aimed at reducing pollution to meet air quality goals, and are continually evolving as computational capacity increases, numerical techniques evolve, the accuracy and resolution of physical and chemical data increases, and as our understanding of atmospheric chemistry and physics increases. However, while AQMs are the best tools currently available for evaluating proposed pollution control strategies, uncertainties in the model components and in input data impact model predictions. Significant progress has been made on uncertainty analysis [(Tonnesen *et al.*, 1998; Russell and Dennis, 2000) and as discussed further in Chapter 4], however some serious concerns remain and simulation results must always be evaluated with the knowledge that the predictions are our best estimates and not a direct representation of atmospheric behavior.

A set of models has emerged over the years that have been well evaluated against historic pollution episodes and have been used for analysis of air pollution control options. These models are known by their acronyms, such as CMAQ, CAMx, UAM, and URM. One model, the Urban-to-Regional Multiscale (URM), is applied here for studies evaluating regional scale air quality issues. The URM model and its predecessors (Odman and Russell, 1991; Kumar *et al.*, 1994; Kumar and Russell, 1996) have been widely used for simulating photochemical air pollutant dynamics.

1.4 Structure and Scope of this Thesis

This thesis presents three modeling applications addressing the formation and control of regional ozone and $PM_{2.5}$, followed by an evaluation of integrated regional pollution and transboundary air quality management. The applications provide evaluation of interstate contributions to ozone and particulate matter, the impacts of emissions exceedances from a single power-plant on regional ozone, and of the ozone formation potential of individual volatile organic compounds.

1.4.1 The URM—1ATM Air Quality Model

The applications described here take advantage of recent enhancements in the URM air quality model, including the incorporation of the chemistry and dynamics of primary and secondary aerosols with reactive scavenging processes (URM-1ATM) (Boylan *et al.*, 2002) and the implementation and extension of the Decoupled Direct Method of sensitivity analysis (DDM-3D) (Yang *et al.*, 1997; Boylan *et al.*, 2002; Hakami *et al.*, 2004c). These enhancements enabled the design of these studies, which before would have been too computationally burdensome and/or beyond the capabilities of current models.

URM-1ATM applies finite elements over a variable scale modeling grid to calculate the change in concentration of species *i* with time. Transport and chemistry are accounted for by solving the atmospheric diffusion equation (ADE; Equation 1.1):

$$\frac{\partial c_i}{\partial t} + \nabla \bullet (\mathbf{u} c_i) = \nabla \bullet (\mathbf{K} \nabla c_i) + R_i + Q_i \qquad (1.1)$$

where **u** is a velocity field, **K** is the diffusivity tensor, R_i represents chemical reactions of species *i* with all other species, and Q_i represents net sources of species *i* not accounted

for by boundary conditions. URM-1ATM is coupled with sensitivity analyses using DDM-3D to calculate local sensitivities S_i of model output C_i to specified model inputs or parameters, P_j, (e.g., elevated NO_x emissions.)

$$S_{ij} = \frac{\partial C_i}{\partial P_j} \tag{1.2}$$

The resulting equations are in the same form as the associated ADE equations, allowing for efficient computation. Because the sensitivity coefficient is a local derivative, a linear assumption is made to extrapolate the result for a specific amount of perturbation to P_j. The linear assumption for ozone and $PM_{2.5}$ has been well tested to at least a 30% perturbation in emissions (Yang *et al.*, 1997; Dunker *et al.*, 2002; Odman, 2002b; Odman, 2002a; Hakami *et al.*, 2004c) and the assumption holds in some cases for an even greater extrapolation (Hakami *et al.*, 2004c).

In URM-1ATM, chemistry is treated in both the gas and aerosol phases. Gas phase chemistry is calculated using the SAPRC chemical mechanism with updated isoprene chemistry (Carter, 1990b; Carter, 1995), accounting for the atmospheric oxidation of over 100 reactive organic compounds along with a number of reactive oxygenated and organic nitrate products. Aqueous-phase chemistry is based on reactions in the Reactive Scavenging Module (RSM) (Scott, 1987; Berkowitz *et al.*, 1989), which accounts for heterogeneous reactions, convective cloud processes, and pollutant scavenging. Both primary and secondary particulate matter are segregated in three groups: inert species, inorganic ionic species, and organic carbon (OC), each of which is further segregated into four size bins. Additional details on chemistry, model formulation, and the treatment of aerosol formation, growth, and removal process are provided in Chapter 2, Appendix A, and elsewhere [(Boylan *et al.*, 2002) and references therein].

For the studies presented in this thesis, a multiscale grid was designed to follow pollutant transport and transformation in the eastern half of the United States, with the finest mesh placed over major emission source regions and highly populated areas (Figure 1.3). Emission inventories and meteorological data for this grid were prepared for three meteorological episodes during May, July, and February to capture a variety of seasonal conditions. A part of one of the modeling applications also utilizes the Community Multiscale Air Quality Model (CMAQ) (Byun and Ching, 1999; NOAA/EPA, 2006) applied to an episode in August. A brief description of CMAQ and the August episode are provided in Chapter 3 and elsewhere (Cohan *et al.*, 2005).

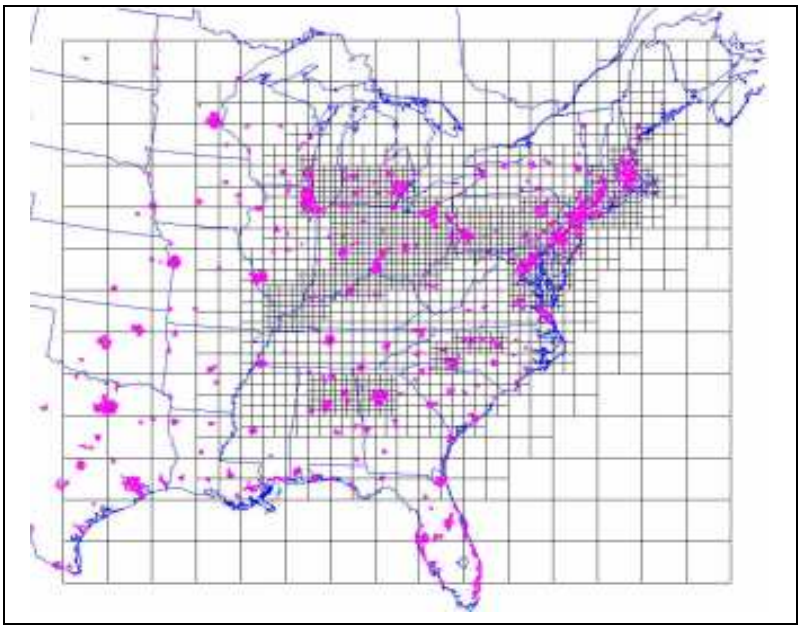


Figure 1.3. Multiscale simulation grid designed for regional control strategy evaluations. Shaded areas are densely populated (urban).

For the URM modeled episodes, the Regional Atmospheric Modeling System (RAMS) (Pielke *et al.*, 1992; Odman, 2002b) was applied in a nonhydrostatic mode, including cloud and rain microphysics, to three nested grids to provide spatially and

temporally resolved meteorological fields. Gridded, hourly, day-specific emissions were estimated using the Emissions Modeling System (EMS-95) (Wilkinson *et al.*, 1994), providing elevated point and ground level source emissions. Ground level emissions are calculated for biogenic, ground level point, area, and mobile sources, some of which are dependent on temperature and solar radiation. Foundation data for point, area, and on-road mobile source emissions were developed by Pechan/Avanti (Pechan, 2001), and point source emissions estimates for major utilities in the domain were refined using utility-provided day specific data (Odman, 2002a; Wilkinson, 2004). Additional emissions and meteorology information is provided in Chapter 2, Appendix A, and elsewhere (Odman, 2002a).

Initial and boundary conditions for air quality, meteorological, and emissions estimates are spatially and temporally resolved. Most gas-phase species of interest rapidly transform or deposit, so are not overly sensitive to IC/BCs, but fine aerosols and ozone can be more persistent and transport further into the domain. Additional information on the data sources and calculation methods for the IC/BCs is available elsewhere (Kumar and Russell, 1996; Boylan *et al.*, 2002).

1.4.2 Chapter Descriptions

- **Chapter 2. Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States.** Impacts of states' emissions on local and interstate ozone and $PM_{2.5}$ concentrations in the eastern United States are analyzed. The URM-1ATM is used to examine the effects of emissions reductions from three source categories in each of 18 states and 4 grouped sets of states on subsequent levels of ozone and secondary $PM_{2.5}$ in each state. Measures of pollution account for both spatial and population-weighted concentrations, and emissions are evaluated on both an equivalent 'per ton' basis and on a 'fractional' basis, which is an

equivalent percentage of each state's estimated emissions. Results from emissions reductions in surface NO_x, such as from motor vehicles; elevated NO_x, such as from power plants and large industrial sources; and total SO_2 emissions are presented. This analysis identifies areas from which emissions are responsible for a significant amount of regional secondary pollution, and areas which do not have independent control over much of their pollution concentrations.

- **Chapter 3. Single-Source Impact Analysis Using 3D Air Quality Models.** The ability to evaluate the impact from a single large emissions source is becoming more important for managing air quality efficiently. Single-source evaluations historically rely on short-range, linear techniques such as dispersion and receptor modeling. However, isolating the impacts of an individual source on secondary pollutants such as ozone and some components of particulate matter must incorporate non-linear processes, be sensitive to small emissions perturbations, and account for impacts that may occur hundreds of kilometers away. Here, a novel policy application is presented utilizing two sensitivity analysis techniques, the Decoupled Direct Method (first and higher-order), and Brute-Force in two detailed regional photochemical models for the evaluation of single-source emissions impacts. This study was performed in support of a recent compliance enforcement action by the US EPA, Department of Justice, and New York, New Jersey and Connecticut (EPA, 2006c) to assess the extent of ozone formed from approximately 2000 to 3000 excess tons of NO_x emissions per month from a single power-plant in Ohio. This lawsuit resulted in a settlement, announced in March 2005, where Ohio Edison will spend $1.1 billion between now and 2012 on various pollution controls to substantially decrease emissions (EPA, 2006c), with an additional $8.5 million civil penalty. In terms of the emissions reductions, cost, and the civil penalty, the settlement is the second largest power plant New Source Review settlement to date (EPA, 2005b).

- **Chapter 4. Impacts of Volatile Organic Compounds on Air Quality and the Development and Expansion of Regulatory Applications Accounting for their Ozone Formation Potentials.** Emissions of volatile organic compounds (VOCs) contribute to tropospheric ozone, exposure to toxic compounds, stratospheric ozone depletion, the accumulation of Persistent Organic Pollutants (POPs) (E-PRTR, 2006), and to secondary organic aerosols. This thesis chapter includes two sections, one addressing the atmospheric impacts of solvents, the second largest emission source of VOCs in many urban airsheds, and the other presenting a review of the technical evolution and cooperative efforts of the scientific, regulated, and regulatory communities in developing regulatory applications accounting for the ozone formation potential of VOCs, along with results from a modeling application addressing regional scale reactivity evaluation and quantification.

  While some states have adopted regulations accounting for reactivity (notably California), there have been significant obstacles to devising reactivity scales for use over a regional area. Advancements supporting the development of regional reactivity policy for ozone control are presented in the second part of this chapter, including development of metrics for quantification, reduction of uncertainty, industry-specific reactivity evaluation, and analysis of ozone impacts on a regional scale.

- **Chapter 5. Regional Atmospheric Pollution and Transboundary Air Quality Management.** A broad discussion of regional atmospheric pollution and transboundary air quality management follows the modeling application chapters. First, regional atmospheric transport and chemistry are presented, as well as the impacts, chemistry, and physics of several significant regional air pollutants (acid deposition, tropospheric ozone, particulate matter, mercury, and POPs). These pollutants are first presented individually, and then some of their linkages with regional climate change and with each other are

addressed. After this scientific background, previous and ongoing efforts to cooperatively characterize and manage regional pollution are examined, and some recommendations for future cooperative policy efforts are presented. Although there is still much to be learned about the regional nature of different air pollutants, our current scientific understanding recognizes that transboundary air pollution is common and that political cooperation is necessary for mitigating the health and environmental damage from these pollutants, and further suggests that future management efforts must recognize both the linkages across geographic scales and between pollutants.

- **Chapter 6. Conclusions and Recommendations for Future Research.** In this chapter, findings of the modeling applications and research are summarized with recommendations for future research. In particular, the modeling applications show that (1) interstate transport of emissions and pollutants is significant, (2) large, single source impacts on secondary pollutants can be evaluated on a regional scale using recently extended sensitivity techniques, and (3) collaborative efforts in regulatory design have resulted in powerful, flexible tools for the regulatory community for accounting for the ozone formation potentials of volatile organic compounds. In addition, regional atmospheric pollution and transboundary pollution mitigation programs are evaluated, with recommendations for the development of future cooperative efforts.

REFERENCES

AMS (1999). American Meteorological Society. "History of the Clean Air Act". http://www.ametsoc.org/sloan/cleanair/index.html (Accessed: Oct., 2006).

Bergin, M.S. and Milford, J.B. (2000). "Application of Bayesian Monte Carlo analysis to a Lagrangian photochemical air quality model." *Atmospheric Environment* **34**(5): 781-792.

Bergin, M.S., Noblet, G.S., Petrini, K., Dhieux, J.R., Milford, J.B. and Harley, R.A. (1999). "Formal uncertainty analysis of a Lagrangian photochemical air pollution model." *Environmental Science & Technology* **33**(7): 1116-1126.

Bergin, M.S. and Russell, A.G. (2001). Organic Solvent Impacts on Tropospheric Air Pollution. In Handbook of Solvents. G. Wypych. New York, ChemTec**:** 1188-1200.

Bergin, M.S., Russell, A.G., Carter, W.P.L., Croes, B. and Seinfeld, J.H. (1998). VOC Reactivity and Urban Ozone Control. In Encyclopedia of Environmental Analysis and Remediation. J. W. Sons. New York**:** 3355-3383.

Bergin, M.S., West, J.J., Keating, T.J. and Russell, A.G. (2005). "Regional atmospheric pollution and transboundary air quality management." *Annual Review Of Environment And Resources* **30**: 1-37.

Berkowitz, C., Easter, R. and BC, S. (1989). "Theory and results from a quasi-steady-state precipitation-scavenging model." *Atmospheric Environment* **23**(7): 555-1571.

Boylan, J.W., Odman, M.T., Wilkinson, J.G., Russell, A.G., Doty, K.G., Norris, W.B. and McNider, R.T. (2002). "Development of a comprehensive, multiscale "one-atmosphere" modeling system: application to the Southern Appalachian Mountains." *Atmospheric Environment* **36**(23): 3721-3734.

Brunekreef, B. and Holgate, S.T. (2002). "Air pollution and health." *The Lancet* **360**(9341): 1233-1242.

Byun, D.W. and Ching, J.K.S. (1999). Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. . U.S. Environmental Protection Agency, Office of Research and Development. Washington, D.C.

CARB and ALA (2004). Recent Research Findings: Health Effects of Particulate Matter and Ozone Air Pollution. CA Air Resources Board and the American Lung Association of CA. http://www.arb.ca.gov/research/health/fs/pm-03fs.pdf

Carter, W.P.L. (1990). "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic-Compounds." *Atmospheric Environment Part a-General Topics* **24**(3): 481-518.

Carter, W.P.L. (1995). "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic-Compounds." *Atmospheric Environment* **29**(18): 2513-2527.

Census (2002). U.S. Census Bureau. "Population Estimates". http://eire.census.gov/popest/data/states/tables/NST-EST2003-01.php (Accessed: March, 2004).

Chang, S.Y. and Allen, D.T. (2006). "Atmospheric chlorine chemistry in southeast Texas: Impacts on ozone formation and control." *Environmental Science & Technology* **40**(1): 251-262.

Cohan, D.S., Hakami, A., Hu, Y. and Russell, A.G. (2005). "Nonlinear Response of Ozone to Emissions: Source Apportionment and Sensitivity Analysis." *Environ. Sci. Technol.* **39**(17): 6739-6748.

Dunker, A.M., Yarwood, G., Ortmann, J.P. and Wilson, G.M. (2002). "The decoupled direct method for sensitivity analysis in a three-dimensional air quality model - Implementation, accuracy, and efficiency." *Environmental Science & Technology* **36**(13): 2965-2976.

E-PRTR (2006). The European Pollutant Release and Transfer Register. Munich, Germany. "Diffuse Sources". http://www.bipro.de/__prtr/sub/database_air.htm (Accessed: Oct., 2006).

EPA. (1997). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. The Benefits and Costs of the Clean Air Act, 1970 to 1990. Final report to the U.S. Congress EPA 410/R-97-002. Available at http://www.epa.gov/air/sect812/copy.html

EPA (2005). U.S. Environmental Protection Agency. "Press Release". http://www.epa.gov/compliance/resources/cases/civil/caa/ohioedison.html (Accessed: June, 2006).

EPA (2006a). U.S. Environmental Protection Agency. "Air Pollution Effects". http://www.epa.gov/ebtpages/airairpollutioneffects.html (Accessed. Oct., 2006)

EPA (2006b). U.S. Environmental Protection Agency. Support Center for Regulatory Atmospheric Modeling. "Air Quality Models". http://www.epa.gov/scram001/aqmindex.htm (Accessed: Feb., 2006).

EPA (2006c). "Ohio Edison Company, W.H. Sammis Power Station, Clean Air Act Settlement". http://www.epa.gov/compliance/resources/cases/civil/caa/ohioedison.html (Accessed: Feb., 2006).

EPA, U.S. (2002). Air Trends. OAQPS. In Highlights. http://www.epa.gov/air/airtrends/aqtrnd02/2002_airtrends_final.pdf. (Accessed Nov., 2006)

FACA (1998). Final Report. Federal Advisory Committee Act Subcommittee for Ozone, Particulate Matter, and Regional Haze Implementation Programs. Co-chairs: John Seitz and Alan Krupnick. Submitted by: Science Applications International Corporation and EC\R, Inc. Submitted to: Air Quality Strategies and Standards Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Division. Research Triangle Park, NC. http://www.epa.gov/ttn/faca/suissu.html

Fiore, A.M., Jacob, D.J., Field, B.D., Streets, D.G., Fernandes, S.D. and Jang, C. (2002). "Linking ozone pollution and climate change: The case for controlling methane." *Geophysical Research Letters* **29**(19).

Frumkin, H. (2002). "Urban sprawl and public health." *Public Health Reports* **117**(3): 201-217.

Hakami, A., Odman, M.T. and Russell, A.G. (2004). "Nonlinearity in atmospheric response: A direct sensitivity analysis approach." *Journal of Geophysical Research-Atmospheres* **109**(D15).

IPCC (2001). Climate Change 2001: Synthesis Report. Summary for Policymakers. Third Assessment. Intergovernmental Panel on Climate Change. http://www.ipcc.ch/

Knipping, E.M. and Dabdub, D. (2003). "Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone." *Environmental Science & Technology* **37**(2): 275-284.

Kumar, N., Odman, M.T. and Russell, A.G. (1994). "Multiscale air quality modeling: application to southern California." *Journal of Geophysical Research* **99**(D3): 5385-5397.

Kumar, N. and Russell, A.G. (1996). "Multiscale air quality modeling of the Northeastern United States." *Atmospheric Environment* **30**(7): 1099-1116.

Lewis, J. (1985). The Birth of the EPA. EPA Journal, Environmental Protection Agency. **Nov**.

NOAA/EPA (2006). "The Community Multiscale Air Quality model (CMAQ)." http://www.epa.gov/asmdnerl/CMAQ/cmaq_model.html (Accessed: Oct., 2006)

NRC (1991). Rethinking the Ozone Problem in Urban and Regional Air Pollution. Washington, D.C., National Research Council, National Academy Press.

NRC (2004). Air Quality Management in the United States. Washington D.C., National Research Council, National Academy Press.

Odman, M.T., Boylan, J.W., Wilkinson, J.G. Russell, A.G., Mueller, S.F., Imhoff, R.E., Doty, K.G., Norris, W.B., McNider, R.T. (2002a). SAMI Air Quality Modeling Final Report. Southern Appalachian Mountains Initiative (SAMI) Governing Body. Ashville, NC.

Odman, M.T., J.W. Boylan, J.G. Wilkinson, A.G. Russell, S.F. Mueller, R.E. Imhoff, K.G. Doty, W.B. Norris, R.T. McNider (2002b). "Integrated modeling for air quality assessment: The Southern Appalachians Mountains initiative project." *J. Phys. IV France* **12**: 211-234.

Odman, M.T. and Russell, A.G. (1991). "Multiscale Modeling of Pollutant Transport and Chemistry." *Journal of Geophysical Research-Atmospheres* **96**(D4): 7363-7370.

Pechan (2001). Southern Appalachian Mountains Initiative (SAMI) emissions projections to 2010 and 2040: growth and control data and emission estimation methodologies. Pechan/Avanti Group.

Percival, R.V., Miller, A.S., Schroeder, C.H. and Leape, J.P. (1996). Ch. 6. Air Pollution Control. In Environmental Regulation: Law, Science, and Policy, Aspen Law & Business.

Pielke, R.A., Cotton, W.R., Walko, R.L., Tremback, C.J., Lyons, W.A., Grasso, L.D., Nicholls, M.E., Moran, M.D., Wesley, D.A. and Lee et, a. (1992). "A comprehensive meteorological modeling system-RAMS." *Meteorology and Atmospheric Physics* **49**(1-4): 69-91.

Russell, A. and Dennis, R. (2000). "NARSTO critical review of photochemical models and modeling." *Atmospheric Environment* **34**(12-14): 2283-2324.

Scott, B. (1987). User's Manual for the Convective Cloud Module Version 1.0. PNL-6188. Pacific Northwest Laboratory. Richland, WA.

Tanaka, P.L., Riemer, D.D., Chang, S.H., Yarwood, G., McDonald-Buller, E.C., Apel, E.C., Orlando, J.J., Silva, P.J., Jimenez, J.L., Canagaratna, M.R., et al. (2003). "Direct evidence

for chlorine-enhanced urban ozone formation in Houston, Texas." *Atmospheric Environment* **37**(9-10): 1393-1400.

Tingey, D.T., Olszyk, D.M., Herstrom, A.A. and Lee, E.H. (1994). Chapter 6. Effects of Ozone on Crops. In Tropospheric Ozone: Human Health and Agricultural Impacts. D. J. McKee. Boca Raton, FL, CRC Press/Lewis Publishers**:** 175–206.

Tonnesen, G., Olaguer, J., Bergin, M., Russell, T., Hanna, A., Makar, P., Derwent, D. and Wang, Z. (1998). Air Quality Models. Relative Reactivity Working Group. http://www.narsto.org/section.src?SID=10

WHO (2004). World Health Organization. "Children's environmental health: Outdoor Air Pollution". http://www.who.int/ceh/risks/cehair/en/ (Accessed: Dec., 2004).

Wilkinson, J.G. (2004). Personal communication.

Wilkinson, J.G., Loomis, C.F., McNally, D.E., Emigh, R.A. and Tesche, T.W. (1994). Technical Formulation Document: SARMAP/LMOS Emissions Modeling System (EMS-95). AG-90/TS26 & AG-90/TS27. Alpine Geophysics. Pittsburgh, PA.

Yang, T., Matus, K., Palsev, S. and Reilly, J. (2005). Economic Benefits of Air Pollution Regulation in the USA: An Integrated Approach. Revision from 2004. MA Instit. of Technol. Cambridge, MA.

Yang, Y.J., Stockwell, W.R. and Milford, J.B. (1995). "Uncertainties in Incremental Reactivities of Volatile Organic-Compounds." *Environmental Science & Technology* **29**(5): 1336-1345.

Yang, Y.J., Wilkinson, J.G. and Russell, A.G. (1997). "Fast, Direct Sensitivity Analysis of Multidimensional Photochemical Models." *Environmental Science & Technology* **31**(10).

CHAPTER 2

REGIONAL AIR QUALITY: Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States

(Michelle S. Bergin, Jhih-Shyang Shih, Alan J. Krupnick, James W. Boylan, James G. Wilkinson, M. Talat Odman, and Armistead G. Russell.
Submitted to *Environmental Science & Technology*)

Abstract

While the U.S. air quality management system is largely designed and managed on a state level, many critical air quality problems are now recognized as regional. In particular, concentrations of two secondary pollutants, ozone and particulate matter, are often above regulated levels and can be dependent on emissions from upwind states. Here, impacts of statewide emissions on concentrations of local and downwind states' ozone and fine particulate matter are simulated for three seasonal periods in the eastern United States using a regional Eulerian photochemical model. Impacts of ground level NO_x (e.g., mobile and area sources), elevated NO_x (e.g., power plants and large industrial sources), and SO_2 emissions are examined.

An average of 77% of each state's ozone and $PM_{2.5}$ concentrations that are sensitive to the emissions evaluated here are found to be caused by emissions from other states. Delaware, Maryland, New Jersey, Virginia, Kentucky, and West Virginia are shown to have high concentrations of ozone and $PM_{2.5}$ caused by interstate emissions. When weighted by population, New York receives increased interstate contributions to these pollutants and contributions to ozone from local emissions are generally higher. When accounting for emission rates, combined states from the western side of the modeling domain and individual states such as Illinois, Tennessee, Indiana, Kentucky, and Georgia are major contributors to interstate ozone. Ohio, Indiana, Tennessee, Kentucky, and Illinois are the major contributors to interstate $PM_{2.5}$. When accounting

for an equivalent mass of emissions, Tennessee, Kentucky, West Virginia, Virginia, and Alabama contribute large fractions of these pollutants to other states.

2.1 Introduction

In 2002, over 50% of the US population lived in counties where monitored air pollution was found to exceed the human health-based national ambient air quality standards (NAAQS). The vast majority of areas that experienced unhealthy air did so because of ozone and particulate matter (Census, 2002; EPA, 2002a). States have struggled to control their air quality for decades, particularly to reduce levels of ozone. In recognition of their widespread effect on human health, the U.S. EPA added NAAQS for particulates with aerodynamic diameters of 2.5 μm and less ($PM_{2.5}$)(EPA). Ambient measurements of $PM_{2.5}$ indicate that concentrations in many areas exceed these standards, and more stringent $PM_{2.5}$ standards have now been proposed.

Historically, the U.S. air quality control regulatory structure treats air quality issues in each state relatively independently by requiring states with areas not attaining the NAAQS to submit State Implementation Plans (SIPs), documenting the steps that will be taken to bring these areas into attainment. Each state controls emissions within its borders in an attempt to hold their pollutant concentrations below the federal standards. However, major components of air pollution are now recognized as both local/urban and regional scale phenomenon (Bergin *et al.*, 2005), meaning that some pollutants can be impacted by interstate transport of pollutants and/or precursors over which receptor states have less control. While regionally-driven regulatory programs are being or have been developed, such as SO_2 emissions trading for electric utilities, the NO_x SIP call, the Clean Air Interstate Rule, and the Clean Air Mercury Rule, a recent National Research Council report concludes that structural changes in the U.S. regulatory system are needed to address the regional component of air pollution (NRC, 2004). Greater understanding of the regional scale relationships between emissions and pollutant concentrations is needed

to develop efficient regulatory programs, would provide more options and flexibility in designing control plans to meet federal goals, and is also important in support of international cooperative efforts in pollution mitigation (Bergin *et al.*, 2005).

Ozone (O_3) is a 'secondary' gas phase compound formed in the atmosphere through chemical reactions. Particulates, also referred to as aerosols, are both 'primary' (directly emitted), such as elemental carbon and soil dust, and secondary mixtures made up of sulfate, organic carbons, nitrate, ammonium, and other species. Precursors for ozone are nitrogen oxides (NO_x) and volatile organic compounds (VOCs), which react in the presence of sunlight. Major secondary particulate precursors are sulfur dioxide (SO_2), NO_x, VOCs, and ammonia. Ozone and particulates share some major precursor sources, providing opportunity for reducing both pollutant concentrations with the same control strategy. However, chemical composition and spatial and temporal patterns of emission must be accounted for in identifying which emission reductions most effectively reduce air pollution.

The Urban-to-Regional Multiscale – One Atmosphere Model (URM-1ATM) (Boylan *et al.*, 2002) is applied to examine the effects of emissions reductions from 18 states and 4 grouped sets of states on subsequent levels of ozone and secondary $PM_{2.5}$. Effects of reductions from three major emission groups are examined – ground level NO_x, elevated NO_x, and SO_2. Ground level NO_x is largely produced by mobile sources such as cars and trucks and by small industrial facilities. Elevated NO_x and sulfur dioxide emissions are largely produced by power plants and other large industrial sources. These emissions represent the major anthropogenic precursors leading to ozone and $PM_{2.5}$ in this domain. A companion study addresses utility NO_x emissions control costs to identify least-cost air quality management strategies (Shih *et al.*, 2003).

2.2 Method

2.2.1 Modeling Domain and Episodes.

URM-1ATM is a three-dimensional photochemical air quality model based on the earlier Urban-to-Regional Multiscale (URM) model (Odman and Russell, 1991; Kumar *et al.*, 1994; Kumar and Russell, 1996). The multiscale grid designed for this project is comprised of four horizontal grid cell sizes, 24x24 km, 48x48 km, 96x96 km, and 192x192 km (Figure 2.1). The finest cells are placed over major emission source regions where many power plants and large industries are located, such as the Ohio River Valley, and over highly populated regions such as the Northeast corridor. This scheme captures population-related emission sources (e.g. automobile exhaust), as well as major industrial sources, and allows more detailed evaluation of potential population exposure to pollutants. There are seven variable-sized vertical layers between the ground and approximately 13 km in altitude.

Three multi-day episodes are modeled to help capture the effects of meteorological and emissions variability. Two of the episodes, July 9-19 and May 22-29, 1995 are used to evaluate ozone responses to emissions changes, and those two episodes plus February 6-13, 1994 are used to evaluate $PM_{2.5}$ responses. The first two days of model simulation per episode are not used for analysis to ensure that initial conditions do not influence results significantly. These three seasonal episodes were selected because large, quality assured, temporally and spatially resolved air quality, meteorological, and emissions data sets were available for the study periods; they were previously modeled using URM-1ATM but with a different multiscale grid configuration. In aggregate, they

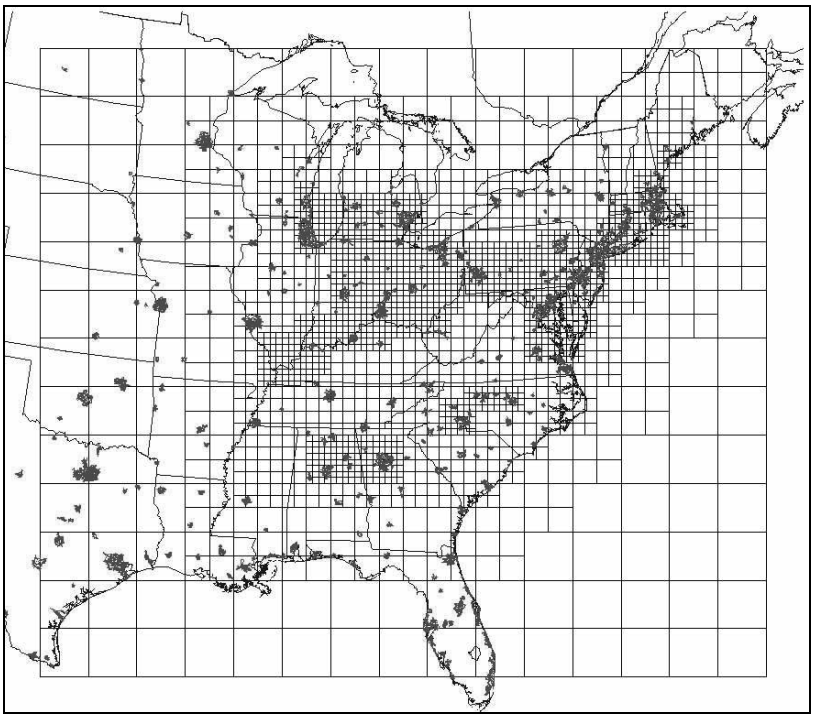


Figure 2.1. Multiscale modeling grid. Shaded areas represent high population densities (urban areas.) Fine scale cells are placed over areas with heavy industry and/or population.

capture a range of meteorological variation that results in both high air pollution events as well as more typical air quality conditions (Boylan *et al.*, 2005). The July episode has hot, sunny conditions that lead to rapid chemistry, increasing photochemical production rates and increasing emissions for some precursors (e.g. mobile source and biogenic organic emissions). A somewhat stagnant atmosphere (i.e., conditions less conducive to transport) allows pollutants to reach high concentrations. Overall, the July episode has higher concentrations and higher sensitivities to emissions reductions for both ozone and $PM_{2.5}$ than do the May or February episodes, so sensitivity results for this episode are more indicative of what controls would be most effective for high pollution events. The May episode represents a cooler, more moderate air quality period, and the February episode provides a winter $PM_{2.5}$ episode. Ozone levels in February are very low (with a maximum 1 hour average of 54 ppbv), so its sensitivity results are not included.

Pollutant responses to emissions reductions are evaluated using projected 2010 emissions scenarios (Figure 2.2) to represent likely conditions under which further control options would be implemented. On this figure and throughout the paper, the acronyms used for the grouped states are simply the state names combined (e.g. DEMD is Delaware and Maryland), except for the grouping termed 'WD', which is the 11 states of the western domain combined (WD = AR + IA + KS + LS + MN + MS + ND + NE + OK + SD + TX). Emissions are projected by accounting for anticipated changes in associated socio-demographic and economic activity, as well as accounting for compliance with current and anticipated emissions regulations. These emissions projections are referred to as 'on the way' and are described in more detail elsewhere (Pechan, 2001; Odman *et al.*, 2002).

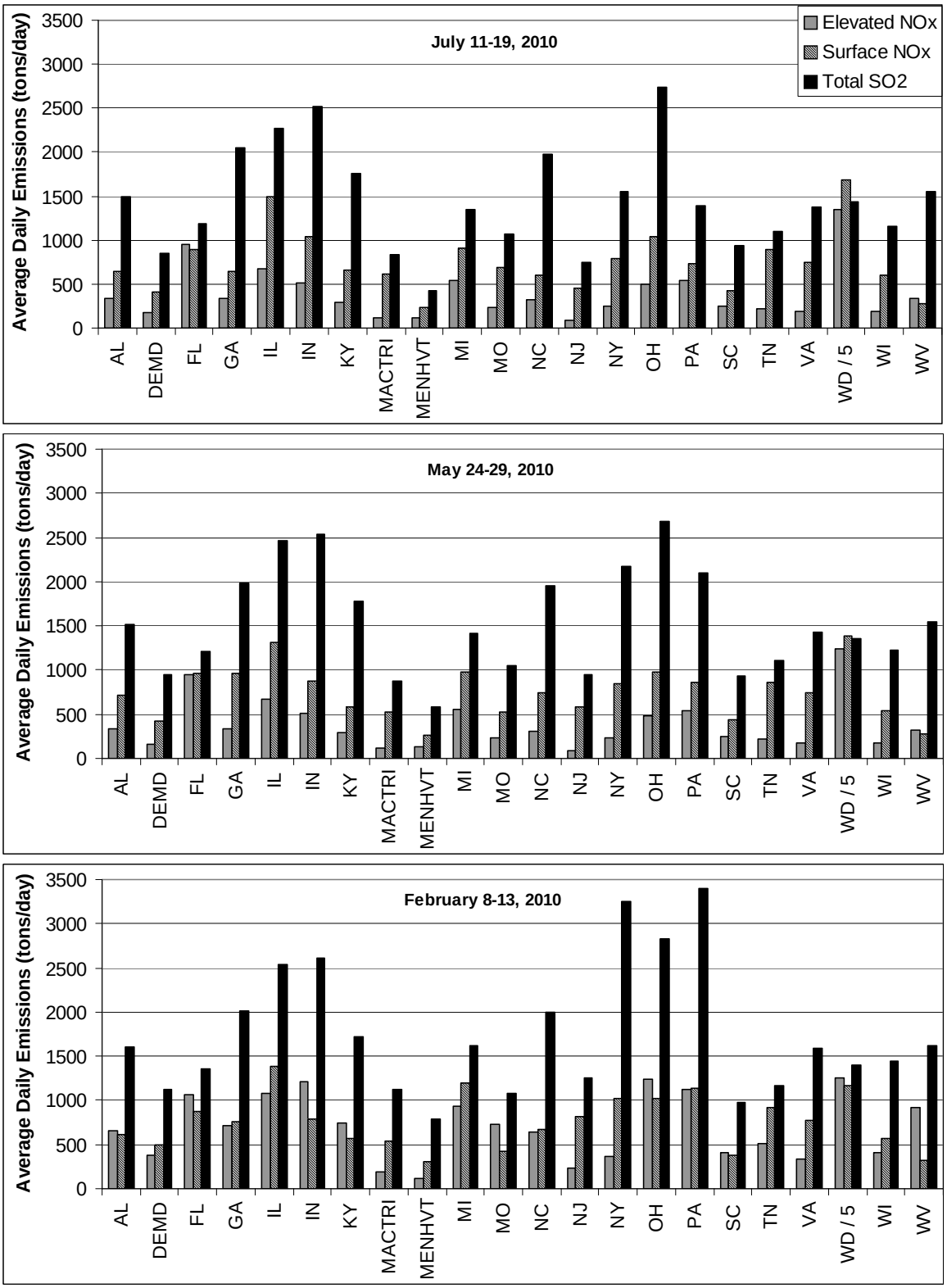


Figure 2.2. Average daily emissions of elevated NO_x, surface NO_x, and total SO_2 per state (tons/day), projected to the year 2010.

2.2.2 Model Description and Data Inputs.

The URM-1ATM simulates the physicochemical dynamics of the atmosphere by solving the atmospheric diffusion equation using finite elements over a variable scale grid. Gas phase species concentrations are calculated using the SAPRC chemical mechanism (Carter, 1990b) with updated isoprene chemistry (Carter, 1995). Aerosol chemistry and dynamics are simulated for primary and secondary organic and inorganic species using four segregated size bins. Inorganic gas-aerosol partitioning is calculated using ISORROPIA (Nenes *et al.*, 1998), and secondary organic aerosols are produced from gas phase reactions using lumped experimental and estimated organic aerosol yields. Mass transfer and particle growth between gas and aerosol species are accounted for by applying condensation and evaporation processes (Pandis *et al.*, 1993), and the Reactive Scavenging Module (RSM) (Scott, 1987; Berkowitz *et al.*, 1989) is incorporated to account for heterogeneous reactions, convective cloud processes, and pollutant scavenging. More details on model description are in Supplemental Information.

Spatially and temporally resolved initial and boundary air quality conditions (IC/BCs), meteorological, and emissions estimates are required inputs to the URM-1ATM. Most gas-phase species of interest rapidly transform or deposit, so are not overly sensitive to IC/BCs, but fine aerosols can be more persistent and transport further into the domain. Information on the data sources and calculation methods for the IC/BCs is described by Boylan et al.(Boylan *et al.*, 2002). The Regional Atmospheric Modeling System (RAMS) (Pielke *et al.*, 1992; Odman, 2002b) is used to derive meteorological fields, and emissions data are calculated using the Emissions Modeling System-95 (EMS-95) (Wilkinson *et al.*, 1994), incorporating emissions projection estimates for the year 2010 (Pechan, 2001). Additional details on data inputs are in Supplemental Information.

The URM-1ATM is coupled with sensitivity analyses using the Decoupled Direct Method in three dimensions (DDM-3D) (Dunker, 1984; Yang *et al.*, 1997; Boylan *et al.*,

2002; Dunker *et al.*, 2002) to calculate local sensitivities S_i of model output C_i to specified model inputs or parameters, P_j, (e.g., elevated NO_x emissions.)

$$S_{ij} = \frac{\partial C_i}{\partial P_j} \tag{2.1}$$

Here, C_i is concentration of ozone or $PM_{2.5}$, and P_j is emissions of SO_2, surface NO_x, or elevated NO_x. Given that the sensitivity coefficient is a local derivative, a linear assumption is made to extrapolate the result. The linear assumption for these pollutants has been well tested to at least a 30% change in emissions (Yang *et al.*, 1997; Dunker *et al.*, 2002; Odman, 2002b; Odman *et al.*, 2002; Hakami *et al.*, 2004c) and the assumption holds in some cases for an even greater extrapolation (Hakami *et al.*, 2004c).

2.3 Results

2.3.1 Model Performance Evaluation.

Model performance for ozone, $PM_{2.5}$, sulfate, and organic carbon aerosol was evaluated for the May and July 1995 episodes. Detailed results are shown in Supplemental Information. Ozone predictions were compared with measurements from the US EPA Aerometric Information Retrieval System (AIRS) (EPA, 2001). Following performance guidelines recommended by the US EPA for urban-scale ozone modeling (EPA, 1991), the average Mean Normalized Bias (MNB) and Mean Normalized Error (MNE) are calculated where observed ozone is greater than 40 ppb (equations shown in Supplemental Information). The results are well within the EPA guidelines for urban scale modeling, which are MNB within ±15% and MNE<35% (EPA, 1991). The overall averaged daily MNB are slightly positive, indicating general over-prediction, and are slightly lower for the July episode (+1.6%) than the May episode (+3.2%). The MNE average is 19.6%.

Aerosol predictions were compared with measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (NPS, 1995), which provides 24-hour averaged data from 11 sites during 5 episode days, and with measurements from a smaller study (the 'Cass study') which provides measurements from 5 sites in NY and MA on July 14, 1995 (Salmon, 1999). The model follows the high and low observed concentration days from the IMPROVE measurements well, and also largely represents the spatial trend of concentration for both the IMPROVE and Cass sites, as shown by high and low predictions at sites with high and low measurements, respectively.

No guidelines are as yet recommended by the US EPA for the quantification of model performance evaluation for aerosols; however, Boylan and Russell (Boylan and Russell, 2006) recommend the use of the Mean Fractional Error (MFE) and Mean Fractional Bias (MFB):

$$MFB_{ar} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left(c_i^m - c_i^o\right)}{\frac{1}{2}\left(c_i^m + c_i^o\right)} \times 100\% \quad (2.2a)$$

$$MFE_{ar} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|c_i^m - c_i^o\right|}{\frac{1}{2}\left(c_i^m + c_i^o\right)} \times 100\% \quad (2.2b)$$

where N is the number of measurements, c_i^m is the modeled concentration of aerosol species *i* in the grid cell co-located with the measurement site, and c_i^o is the observed concentration. MFB ranges from −200% to +200% and MFE ranges from 0% to +200%.

For $PM_{2.5}$ (performance metrics are calculated for reconstructed $PM_{2.5}$, which does not include water), the MFB is typically low, +6% including all days except for May 27 when it is +36%. The $PM_{2.5}$ MFE is 30%. Sulfate is the largest single component of

$PM_{2.5}$ for most measurement sites, particularly on days with high $PM_{2.5}$, and is strongly impacted by emissions evaluated in this study. High and low sulfate days are generally well represented by the model, as is the spatial trend of the concentrations. The Cass sites are all under-predicted, most likely because Canadian point source emissions were not available for this study and Canadian area source emissions are likely underestimated (Wilkinson, 2006). Over the IMPROVE days, the MFB for sulfate ranges from 39% to -18%, and is 0% over all days combined. The MFE is 40%. Organic aerosols tend to be the next most common aerosol component, accounting for roughly a quarter of the $PM_{2.5}$ mass. Modeling of organic aerosols is still highly uncertain; however model performance results for this study were very good, with an overall MFB of +15% and MFE of 40%. July and May 1995 results were compared with those from the prior related study (Boylan *et al.*, 2006) to ensure similar model performance, and results for the February 1994 episode are considered to be similar.

2.3.2 2010 Simulated Pollutant Concentrations and Sensitivities.

Sensitivities of ozone and fine aerosols were calculated using DDM-3D to examine the impact of states' emissions on their own and on other states' air quality. Results from these sensitivity calculations can be quantified in many ways, but in the interests of space and clarity only a selection is presented here and in the Supplemental Information section. Model results for July 17, 2010 show high concentrations of both ozone and $PM_{2.5}$, and high sensitivities of these pollutants to emissions, so results from this day are used to illustrate some relationships between pollutant concentrations and sensitivities as well as differences in some state impacts (Figures 2.3 and 2.4).

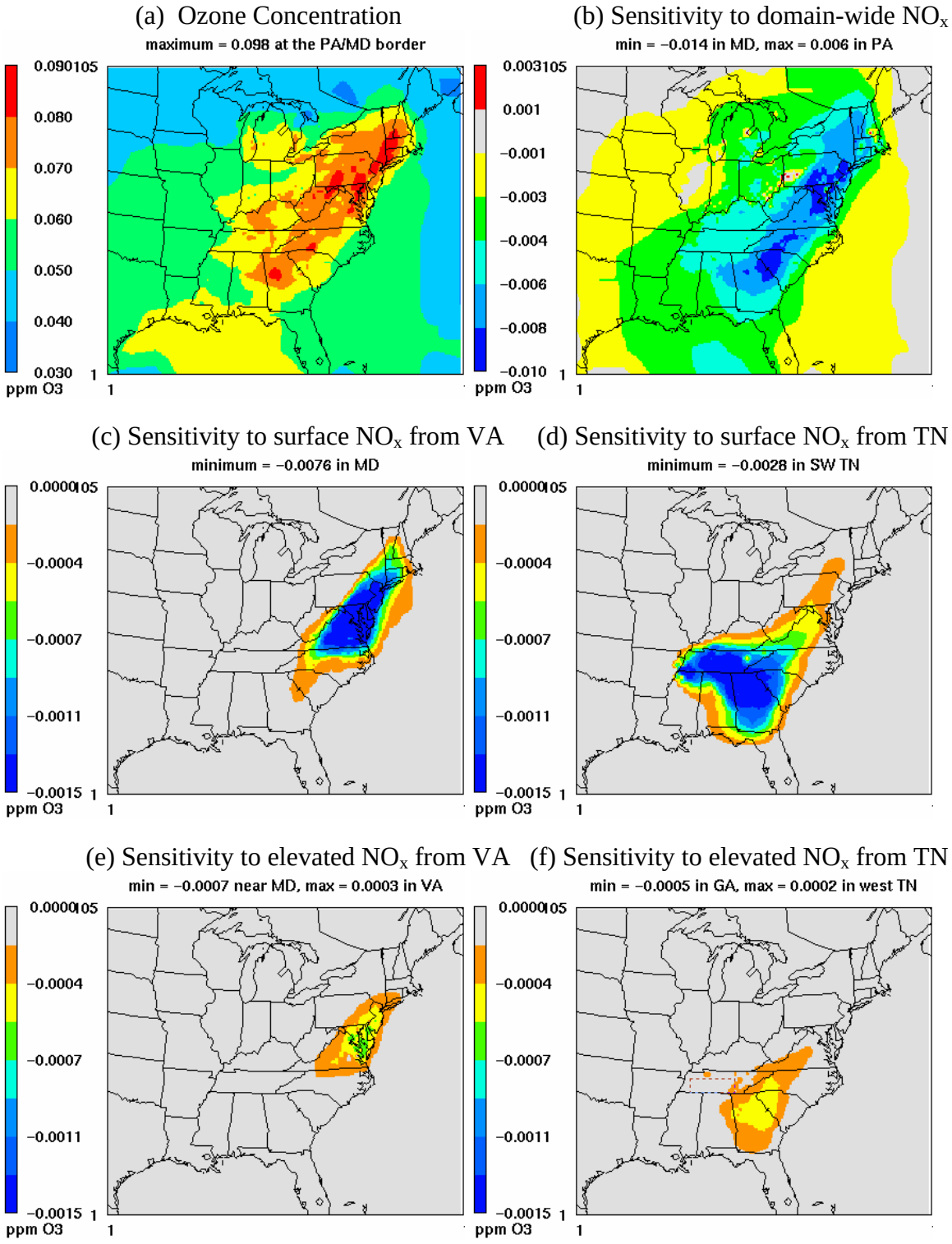


Figure 2.3. (a) Eight-hour averaged ozone concentration and its sensitivity to a 30% reduction in (b) domain-wide NO_x emissions, (c) in surface NO_x emissions from Virginia and (d) from Tennessee, and in (e) elevated NO_x emissions from Virginia and (f) from Tennessee on July 17, 2010 from 11:00 a.m. to 7:00 pm. Negative values represent decreases in ozone.

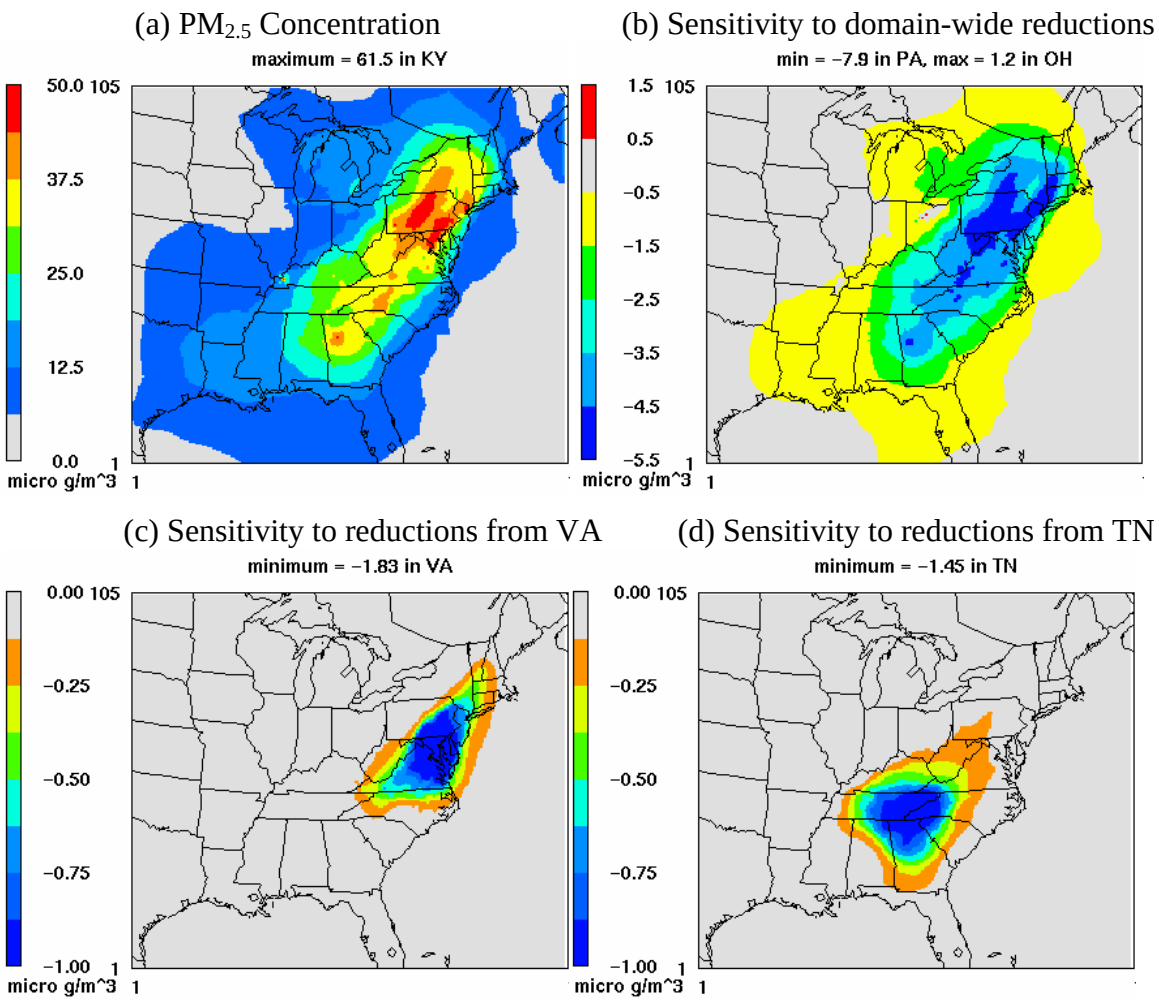


Figure 2.4. (a) Twenty-four hour averaged $PM_{2.5}$ concentration on July 17, 2010 and (b) its sensitivity to 30% reductions in SO_2 , surface NO_x, and elevated NO_x emissions domain-wide, (c) reductions from Virginia, and (d) reductions from Tennessee.

Using 2010 emissions, the 8-hour averaged maximum ozone concentration on July 17 is 0.098 ppm, and occurs between 11:00 am and 7:00 pm on the border between Pennsylvania and Maryland (Figure 2.3a). The sensitivity of ozone for this time period to a 30% reduction in surface NO_x and in elevated NO_x from all source areas in the domain has a maximum decrease of 0.014 ppb in Maryland, very close to the peak concentration, and a maximum increase of 0.006 in Pennsylvania (Figure 2.3b). For a rough estimate, a fully linear extrapolation of this maximum sensitivity to 100% emissions reductions indicates that the emissions tested here are responsible for around 48% of the 8-hour peak

ozone concentration on this day. The ozone response to this level of NO_x reduction would not be linear; however this rough approximation allows the fraction of peak ozone caused by these emissions to be estimated. Accounting for the nonlinear ozone response would most likely increase this estimate as the secondary derivative of ozone sensitivity to NO_x reduction generally estimates an additional reduction in ozone (Hakami *et al.*, 2004c; Cohan *et al.*, 2005). Natural background ozone concentrations have been shown to account for around 15–30 ppbv in the eastern U.S. during the summer of 1995 (Fiore *et al.*, 2002a; Fiore *et al.*, 2003). The remainder of the ozone peak could be due to other contributors, such as anthropogenic precursor emissions sources from outside of the modeling domain and the anthropogenic component of increased global background (Fiore *et al.*, 2003; Vingarzan, 2004). Freshly emitted NO_x reduces ozone under certain conditions near the emission source (e.g. the positive values in Figure 2.3b), however ultimately NO_x emissions increase ozone concentrations, particularly during daylight hours (Bergin *et al.*, 2006a).

The spatial patterns of ozone sensitivity to emissions reductions from each state vary considerably. For example, the greatest impact to predicted surface ozone 8-hour averaged concentrations from a 30% reduction in surface NO_x emissions from Virginia (a reduction of 0.008 ppm) occurs around the Virginia-Delaware-Maryland area (Figure 2.3c). In comparison, a 30% reduction in surface NO_x emissions from Tennessee results in less of a decrease in ozone (0.003 ppm), but has a larger area of impact, reaching Tennessee, Georgia, Alabama, and South Carolina. (Figure 2.3d). 30% reductions in elevated NO_x emissions from these states result in comparable distribution patterns of reduced ozone, but are of a lesser magnitude than from reductions in surface NO_x (Figures 2.3e-f).

The maximum 24-hour average simulated $PM_{2.5}$ concentration on the same day is 61.5 $\mu g/m^3$ in Kentucky (Figure 2.4a). Its sensitivity to a 30% reduction in SO_2, surface NO_x, and elevated NO_x emissions from all source areas in the domain is a maximum

decrease of 7.9 μg/m^3 in Pennsylvania, with a localized maximum increase of 1.2 μg/m^3 in Ohio (Figure 2.4b). A fully linear extrapolation approximation indicates that the emissions accounted for here contribute to roughly 43% of the $PM_{2.5}$ concentration on this day. $PM_{2.5}$ sensitivity to SO_2, the majority of the total sensitivity here, is generally more linear than the ozone sensitivity to NO_x (Russell, 2006) so is likely closer to the actual 100% response than is the ozone estimate above. Although ozone and $PM_{2.5}$ have significant differences in chemistry and precursor sources, 24-hour averaged $PM_{2.5}$ responses exhibit similar spatial patterns to 30% reductions in state NO_x and SO_2 emissions from Virginia and Tennessee (Figure 2.4c-d).

2.3.2.1 Source-Receptor Coefficient (SRC) and Impact Factor (SRIF) Calculations

Aggregate pollution impacts are quantified by calculating source-receptor coefficients (SRCs) and impact factors (SRIFs) for each source-receptor pair by linking the pollutant's maximum sensitivity in each grid cell in the receptor to emissions from each source. Concentrations and sensitivities in 48x48 km grid cells and larger are interpolated to 24x24 km cells for comparative analysis. The sources/receptors are 18 individual states and 4 grouped sets of states. The grouped states are sometimes referred to simply as being a 'state' throughout the paper for brevity.

The SRC is a measure of pollutant sensitivity at a receptor to one ton of emissions from a source (per ton), allowing comparison of the effects of equivalent mass reductions, while the SRIF is the pollutant sensitivity to a 30% reduction in emissions from a source, allowing comparison of the effects of equivalent percentage reductions. The SRC is calculated as:

$$SRC_{rs} = \frac{\sum_{d=1}^{D} \left[\frac{\left(\sum_{i=1}^{N} \left[S_{is}^{\max} \right]_d p_i \right)}{\sum_{i=1}^{N} p_i} \right]}{D} \qquad (2.3)$$

where the receptor *r* is an area represented by *N* number of grid cells, and source *s* is the area where the precursor emissions originate (P_j in eq 2.1). $\left[S_{is}^{\max}\right]_d$ is the pollutant's maximum sensitivity averaged over 8 or 24 hours, for ozone and $PM_{2.5}$ respectively, in receptor cell *i* to the precursor emissions of interest from source *s* during day *d*. When calculating population-weighted SRC_{rs}, p_i is the population of grid cell *i*, and for area-weighted (spatial) SRC_{rs}, p_i is set to 1. The value is averaged over the number of episode days, *D*. Population-weighted SRCs are calculated as an indicator of potential population exposure to the pollutants (activity patterns are not considered). While the Clean Air Act is designed to protect the health of each person equally, it is useful to see what emissions reductions could potentially lead to greater reductions in cumulative human exposure. Units of both spatial- and population-weighted SRC_{rs} are ppt/ton for ozone and ng/m^3/ton for $PM_{2.5}$.

While SRCs are useful for evaluating the impacts of equivalent mass emissions reductions between states, some states have large differences in their total anticipated mass of emissions (Figure 2.2), and, therefore, in how much they are actually able to reduce emissions. To account for this, we also calculate $SRIF_{rs}$ by scaling the SRC_{rs} by source emissions, E_s, which is equal to 30% of the average daily emissions from the source area. Note that a positive SRC or SRIF represents a reduction in pollutant concentration in response to a reduction in emissions.

$$SRIF_{rs} = SRC_{rs} E_s \tag{2.4}$$

Each of these metrics, SRC and SRIF, are calculated for each emission source category and each episode for every source-receptor pair. For ozone, SRCs and SRIFs are calculated to reductions in surface and elevated NO_x emissions for the July and May episodes. For $PM_{2.5}$, SRCs and SRIFs are calculated to reductions in total SO_2, surface

NO_x, and elevated NO_x emissions for the July, May, and February episodes. To the first order, SRIFs can be linearly combined across emission category contributions (e.g. sensitivity of ozone to a 30% reduction of elevated NO_x plus a 30% reduction of surface NO_x). Because ozone is regulated on a daily maximum basis, the July and May episode results are not combined. $PM_{2.5}$ is regulated on an annual average basis, so results for the three episodes are averaged. On a per ton basis, source category contributions cannot be combined, so SRCs are discussed for each emissions category separately.

2.3.2.2 Comparison of Episode and Emissions Category Contributions

Relative contributions to ozone and $PM_{2.5}$ concentrations from each emission category for each episode are compared by averaging SRCs contributed from each source state (Figure 2.5). Overall, the July episode has higher concentrations and higher sensitivities to emissions reductions for both ozone and $PM_{2.5}$, so is most indicative of what reductions would be most effective for high pollution episodes. Regional (out of state) contributions are larger than local (in state) contributions for both pollutants in every episode from every emissions category. For both episodes, surface NO_x is a larger contributor to ozone, although surface and elevated NO_x have similar contributions in May. Considering all episodes together, the largest contribution to $PM_{2.5}$ from the sources comes from SO_2 emissions, followed by surface and then elevated NO_x (Figure 2.5) (note that only SO_2 and NO_x sources are considered). SO_2 emissions in July are clearly the largest source of inorganic $PM_{2.5}$ for these three emissions categories during these episodes. Contributions to $PM_{2.5}$ are more evenly distributed between emissions categories during May and February.

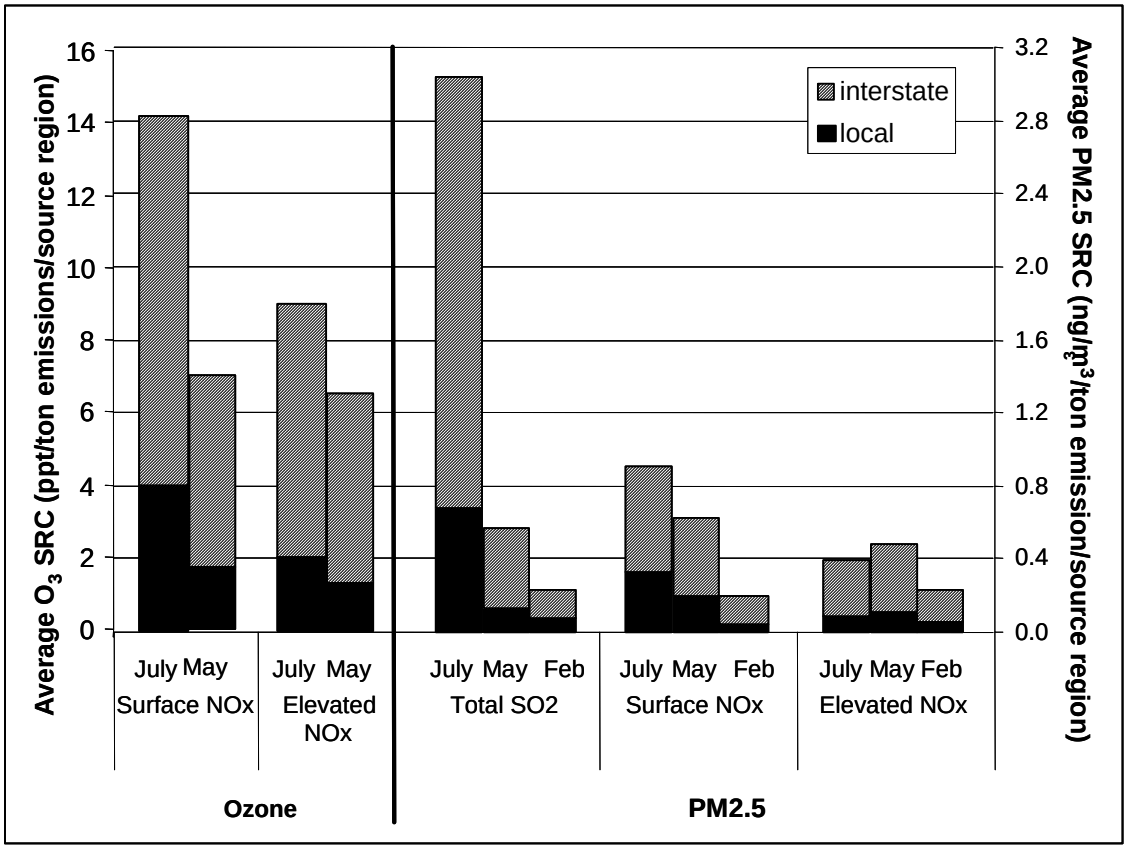


Figure 2.5. Comparison of average contributions from source states to ozone and $PM_{2.5}$ Source Receptor Coefficients for each episode and emissions category.

2.3.2.3 States as Sources

While the averaged source contributions illustrate the relationships between regional and local impacts, source category contributions, and episodes (Figure 2.5), detailed analysis of individual source state contributions to local and interstate ozone and $PM_{2.5}$ show significant variability (Figures 2.6 and 2.7). When ozone sensitivities are based on equivalent tons of NO_x emissions reductions (e.g. SRCs), emission categories and episodes are considered separately. Ozone sensitivities to surface NO_x in July are shown here (Figure 2.6a); results for sensitivity to reductions in elevated NO_x in July and

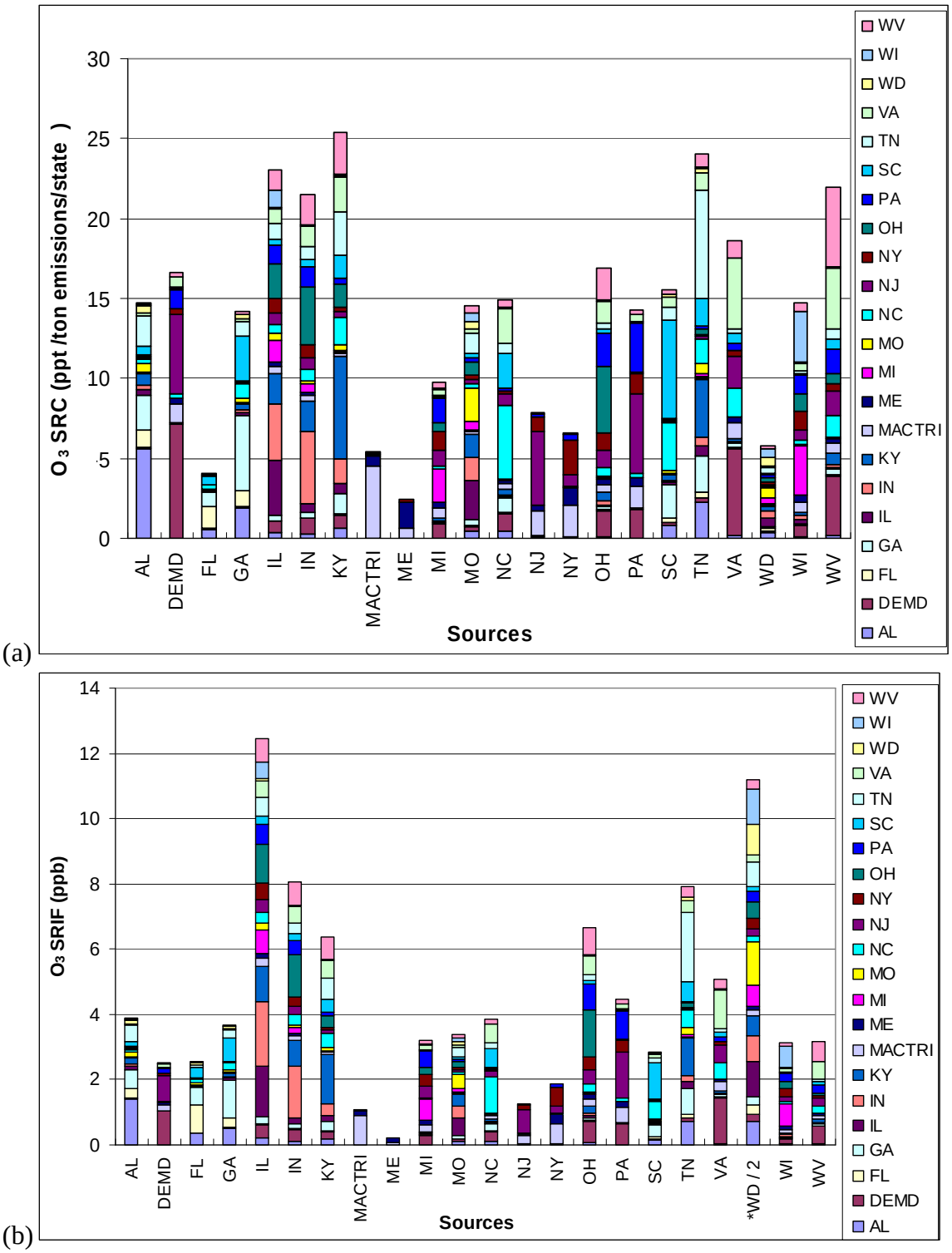
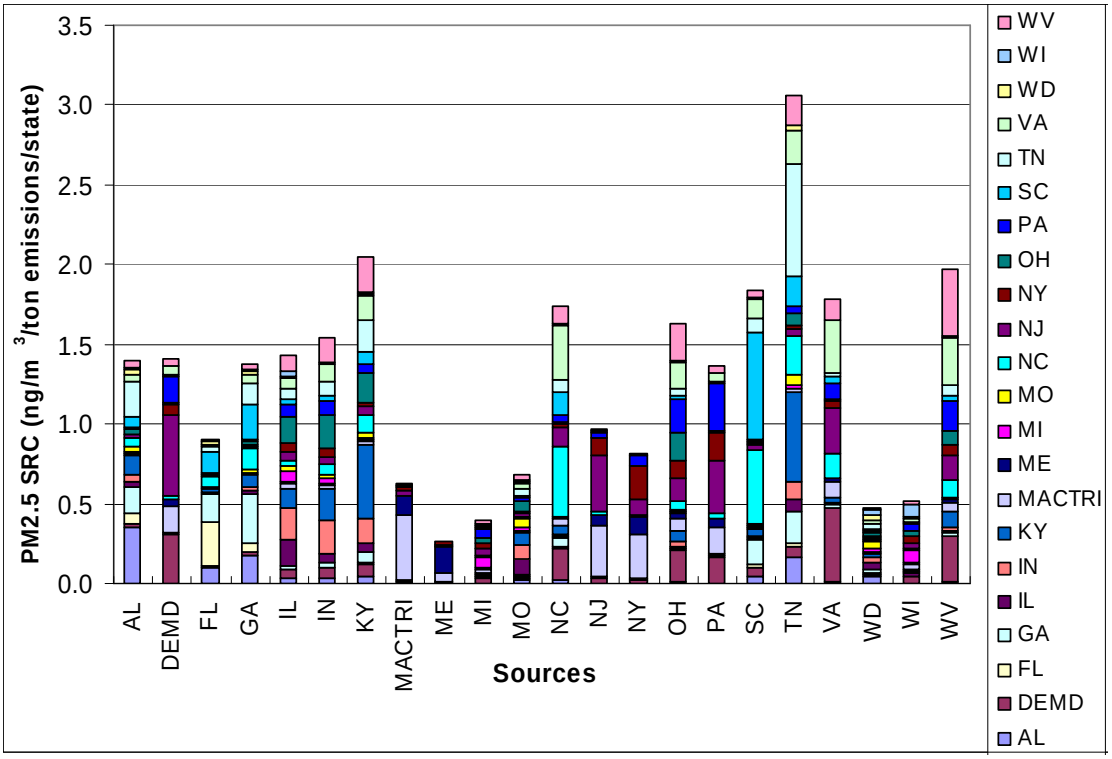


Figure 2.6. Ozone (a) Source Receptor Coefficient contributions from one ton reductions in surface NO_x emissions during the July episode, and (b) Source Receptor Impact Factor contributions from 30% reductions in surface and elevated NO_x emissions during the July episode.

(a)



(b)

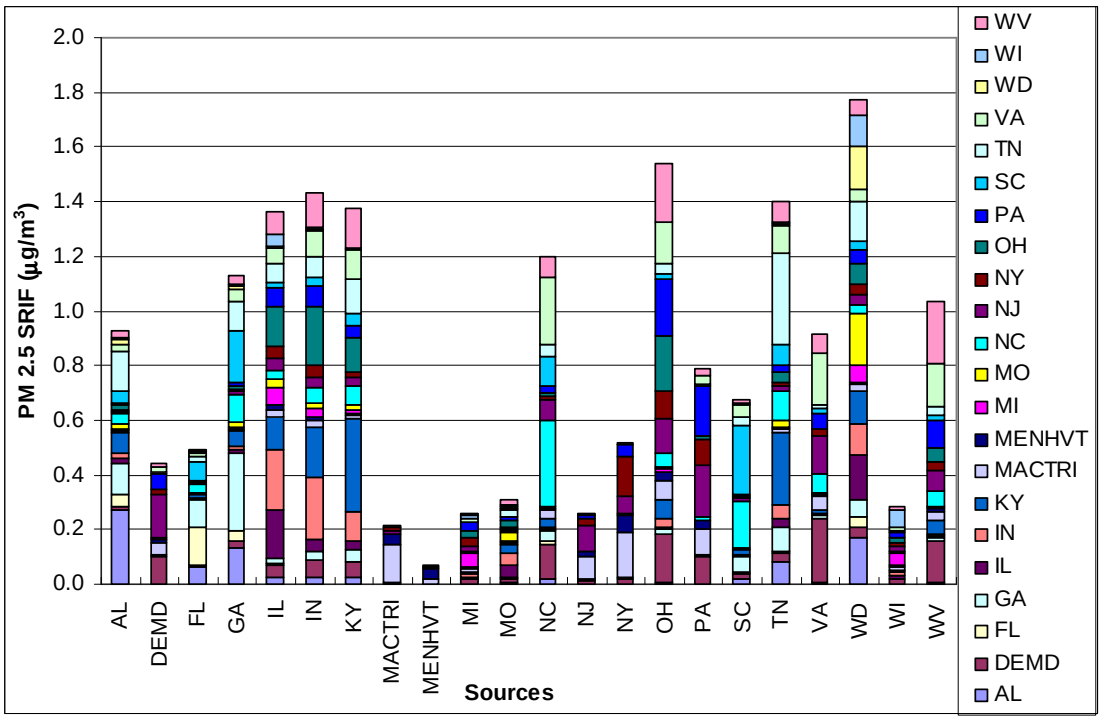


Figure 2.7. $PM_{2.5}$ (a) Source Receptor Coefficient contributions from one ton reductions of SO_2 averaged over the July, May, and February episodes, and (b) Source Receptor Impact Factor contributions from 30% reductions in SO_2, surface, and elevated NO_x emissions averaged over the July, May, and February episodes.

surface NO_x and elevated NO_x in May are in Supplemental Information. Considering both local and regional contributions, Kentucky is the largest "source" state to ozone from surface NO_x, with its largest impacts on itself, Tennessee, and West Virginia. Tennessee is the next largest contributing source state, followed by South Carolina, Alabama, and Virginia. When considering ozone sensitivity to elevated NO_x, emissions from Tennessee are clearly the dominant contributor (Supplemental Information.) When ozone sensitivities are calculated to equivalent fractional reductions in NO_x emissions (e.g. SRIFs), sensitivities to elevated and surface NO_x emissions are added together (Figure 2.6b). Here, due to the large amount of emissions from the 11 combined states (WD; Figure 2.2), WD is the largest contributing source, followed by Illinois. Indiana, Tennessee, Ohio, and Kentucky are also high contributors to regional ozone.

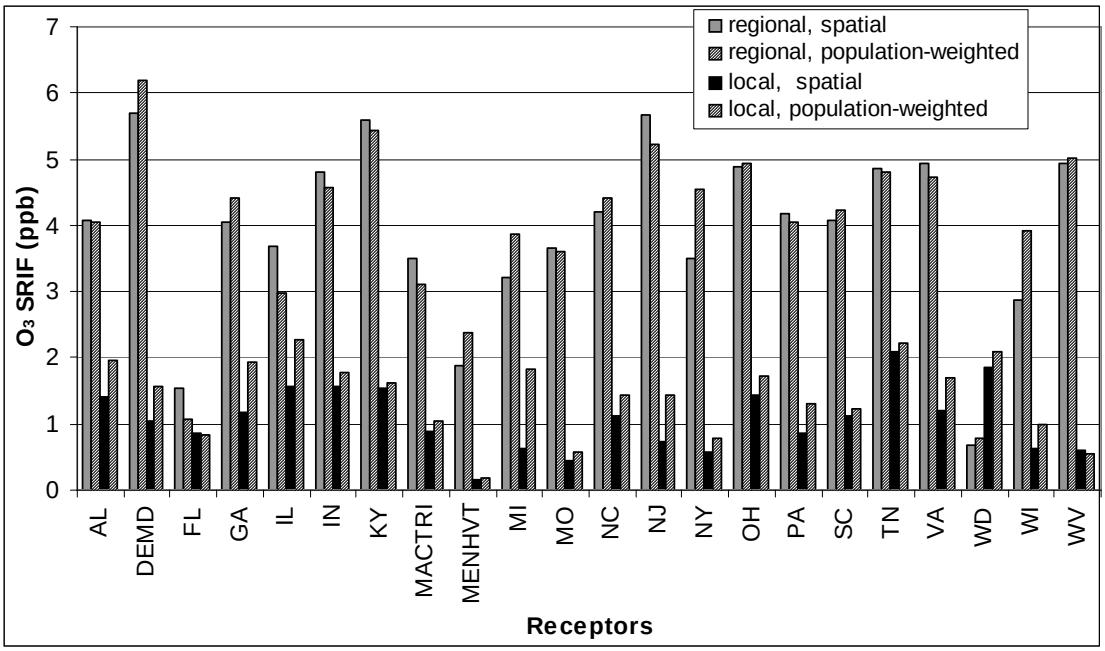
The sensitivity of $PM_{2.5}$ to emissions reductions on both a per ton (e.g. SRC) and equivalent fraction (e.g. SRIF) basis are averaged between the July, May, and February episodes (Figure 2.7). Because sensitivity to SO_2 emissions is greatest, SO_2 results are presented for comparison of equivalent mass emission reductions (e.g. SRCs.), and sensitivities to surface and elevated NO_x are in Supplemental Information. Tennessee is clearly the dominant contributor on a per ton emissions basis (Figure 2.7a), followed respectively by Kentucky and West Virginia. $PM_{2.5}$ sensitivities to surface and elevated NO_x are highest for emissions from Tennessee, Kentucky, and Alabama. When $PM_{2.5}$ is calculated using equivalent fractional emissions reductions (SRIFs; Figure 2.7b), WD is again the dominant contributor, followed by Ohio, Indiana, Tennessee, Kentucky, and Illinois, respectively.

A comparison of segregated regional and local contributions, weighted spatially and by population, to ozone and $PM_{2.5}$ from each source state based on an equivalent percentage reduction of emissions is shown in Supplemental Information.

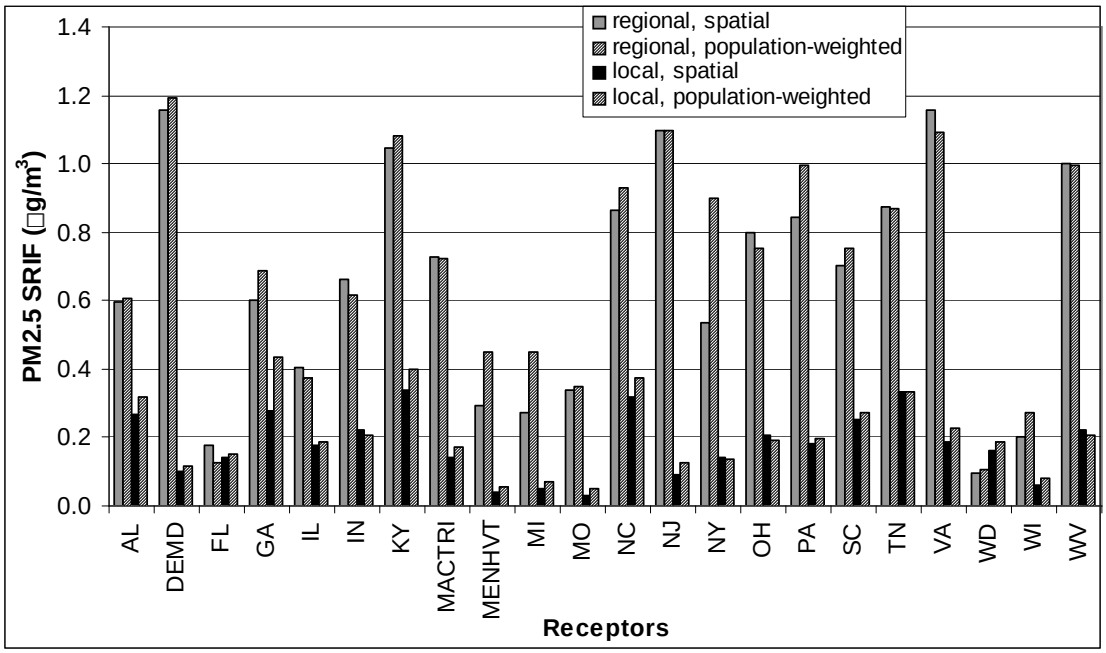
2.3.2.4 States as Receptors

While ozone and $PM_{2.5}$ have differing dominant precursor species and are produced under different conditions, the relative fraction of locally versus regionally contributed components is similar within each state (Figure 2.8). Overall, an average of 72% of both the peak ozone and $PM_{2.5}$ within each state that is sensitive to the emissions evaluated here results from emissions originating in other states. However, some states receive far higher regional contributions to pollutants than others. DEMD receives the highest concentrations of regional ozone and $PM_{2.5}$ in this domain. Concentrations in New Jersey, Virginia, Kentucky, and West Virginia are also strongly dependant on external emissions. Results for ozone sensitivity in May (Supplemental Information) are similar for many states, however a few states show much higher sensitivity to local emissions (e.g. FL, AL, GA), and a few show a negative population-weighted response (ozone increases) to emissions reductions (e.g. IL, MI, NY). Spatial and population weighted measures show fairly similar results for most states, although regional contributions increase significantly when population weighted in New York for both ozone and $PM_{2.5}$, and in Pennsylvania, Michigan, and MANHVT for $PM_{2.5}$. When weighting the sensitivities by population, an average of 71% of ozone and 73% of $PM_{2.5}$ is due to emissions from other states.

The local component of ozone SRIFs tend to increase when weighted by population (e.g. GA, IL, MI, and NJ), primarily due to a larger impact from surface NO_x emissions, which increase with population due to sources such as automobiles. However, the local contribution to ozone is lower when weighted by population in New York due to ozone titration in the NO_x rich atmosphere of the most populated area in New York (i.e. New York City). Population-weighted local and regional ozone SRIFs are also lower than the spatial SRIFs in Illinois likely because there is a high population density (e.g. Chicago) near Lake Michigan, and biogenic VOC emissions and mixing depths tend to be



(a)



(b)

Figure 2.8. Comparison of spatial and population-weighted Source Receptor Impact Factors in each receptor state from local and regional sources for (a) 8-hour ozone sensitivity to 30% reductions in surface and elevated NO_x emissions combined during the July episode, and (b) daily $PM_{2.5}$ sensitivity to 30% reductions in SO_2 and surface and elevated NO_x emissions, averaged over the July, May, and February episodes.

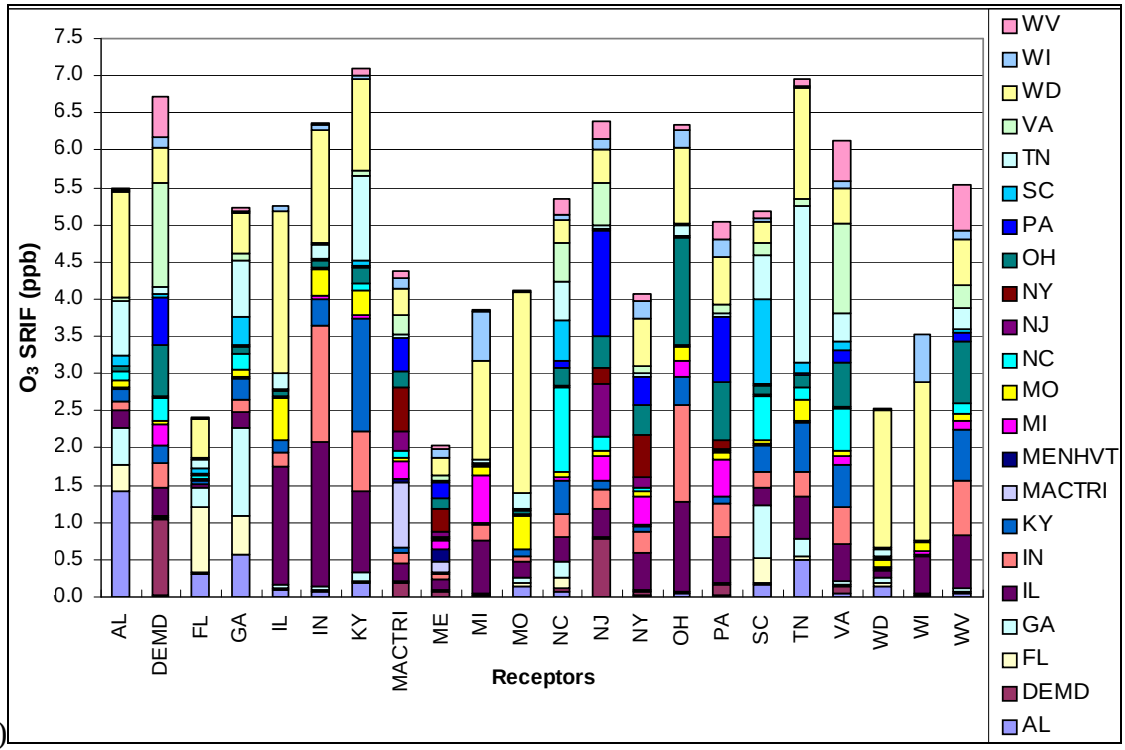
low. Because the VOC concentrations are low, NO_x emissions can titrate ozone, leading to an increase in ozone from a decrease in NO_x emissions. The local component of $PM_{2.5}$

tends to increase with population weighting, particularly in Georgia where the high population density (i.e. Atlanta) is far from the state borders. As with ozone, regional contributions to $PM_{2.5}$ in New York increase significantly when population-weighted, primarily due to increased weighting of impacts from emissions from New Jersey and Pennsylvania. Regional contributions to $PM_{2.5}$ also increase with population weighting in MANHVT, Michigan, and Pennsylvania.

Pollutant sensitivities in each state to 30% reductions in emissions (e.g. SRIFs) are examined in more detail by showing the individual contributions from each source state to each receptor state (Figure 2.9). Because the local component is added in this figure, Kentucky and Tennessee (rather than DEMD and NJ) now show the highest overall ozone SRIFs in July (each of the receptor columns in Figure 2.9 include the sum of the local and regional spatially weighted columns in Figure 2.8). These states are followed by DEMD, New Jersey, Ohio, and Indiana. In May, DEMD and Virginia are the highest receptors, followed by West Virginia (Supplemental Information). High local plus regional $PM_{2.5}$ SRIFs for the combined episodes are found for Kentucky, Virginia, DEMD, West Virginia, New Jersey, and North Carolina (Figure 2.9b). WD is not particularly sensitive to the interstate emissions evaluated here, as dominant wind patterns are from west to east and boundary conditions are held constant.

Receptor state impacts from equivalent mass reductions in emissions (SRCs) show similar results for SRIFs of both ozone and $PM_{2.5}$ (Supplemental Information). However, Kentucky and Tennessee do not show dominant ozone sensitivity to 'per ton' emissions reductions in July. SRCs for $PM_{2.5}$ are even more similar to SRIFs than are those for ozone. Much of the difference between SRIF and SRC results is because states with high emissions are heavily weighted, such as WD. A few states show ozone increases in response to NO_x reductions (i.e. negative SRCs), particularly when weighting

(a)



(b)

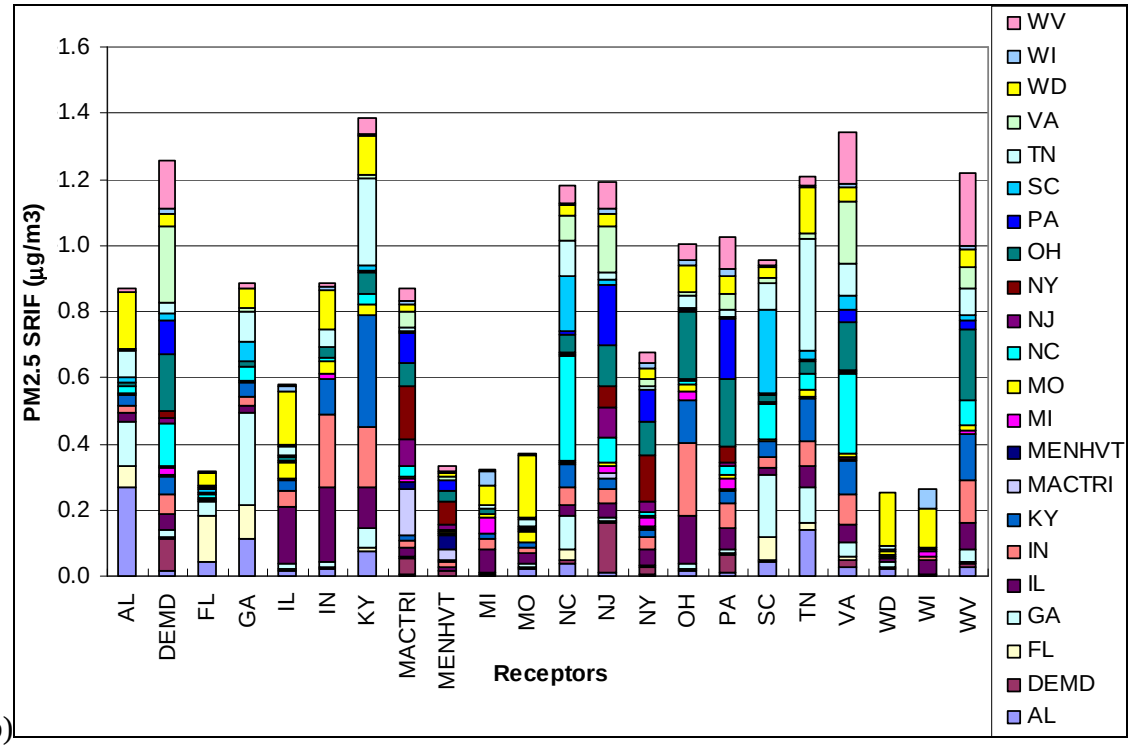


Figure 2.9. Source Receptor Impact Factors in each state for (a) ozone sensitivity to 30% reductions in surface and elevated NO_x emissions during the July episode, and for (b) $PM_{2.5}$ sensitivity to 30% reductions in SO_2, surface, and elevated NO_x emissions averaged over the July, May, and February episodes.

sensitivities by population and during the May episode (Supplemental Information).

2.3 Discussion

Although the dominant precursors for ozone and $PM_{2.5}$ for the region examined here are different (NO_x for ozone and SO_2 for $PM_{2.5}$), most of the source states causing high regional impacts are found to be the same for both pollutants (Figures 2.6 and 2.7, also Supplemental Information). When sensitivities are compared based on reductions in an equivalent mass versus equivalent fraction of emissions (e.g. SRCs v. SRIFs), the dominant contributing states change somewhat, offering different implications for policy decisions depending on priorities. Based on the receptor criteria applied here, emissions reductions in states with high contributions based on equivalent fractions of emissions (e.g. high contributing SRIFs) would be most effective at reducing anticipated ozone and $PM_{2.5}$ concentrations. Incentives for controlling development or growth of emissions may be indicated for states exhibiting high contributions to ozone and $PM_{2.5}$ based on equivalent mass of emissions (e.g. high SRCs).

In general, states that receive high regional ozone also receive high regional $PM_{2.5}$ on both a spatial and population-weighted basis (Figure 2.8). These heavily impacted states are usually not dominant source states, so have limited options available for in-state emissions reductions and may need to consider other strategies for controlling local pollutant concentrations. A companion paper explores some economic ramifications of these relationships and presents a number of optimal control scenarios for elevated NO_x emissions from electric generating utilities under different constraining goals (Shih *et al.*, 2003).

As with all modeling studies, the results for these simulations must be considered while acknowledging uncertainty and variability (Oreskes *et al.*, 1994; Russell and Dennis, 2000; Fine *et al.*, 2003). Additionally, while these three episodes indicate which

states are major contributors and receptors of daily average $PM_{2.5}$ for these periods, local and interstate impacts on annual average $PM_{2.5}$ concentrations should be evaluated for a number of years. Also, as more information is gained on the sources and formation of organic aerosols, the spatial relationship of this important component of $PM_{2.5}$ with its sources should also be evaluated.

The complexity of these interstate relationships between emissions and pollutant concentrations has important ramifications for air quality control decisions by state and federal policy makers. An average of approximately three-quarters of states' ozone and $PM_{2.5}$ concentrations are found to result from out-of-state emissions for the episodes and emissions examined here, which roughly account for nearly half of the peak ozone and $PM_{2.5}$ concentrations evaluated. Correspondingly, on average, each state's emissions cause a similar total fraction of pollution in other states. This situation presents a strong incentive for regional collaboration, at a minimum scale, for more efficient and cost-effective pollution control options than those currently available if states act individually. These result support a number of mechanisms that have been proposed to better facilitate overall air quality management in the United States on an even larger spatial scale [e.g.(Holloway *et al.*, 2003; NRC, 2004; Shih, 2004; Bergin *et al.*, 2005)], to offer more efficient control of certain long-range pollutants (including those effecting climate) and to offer more efficient use of emissions control from large source categories (e.g. power-plants and mobile sources), and to aid international efforts in cooperative pollution mitigation.

Acknowledgments

Funding was provided through an EPA/NSF Partnership Grant under US EPA STAR Grant R825821, and through a US EPA STAR Graduate Fellowship. Partial funding was also provided under US EPA grants RD82897602, RD83107601, and

RD83096001. The opinions, findings, conclusions, and recommendations are those of the authors and do not necessarily represent the views of the EPA or NSF. The EPA and NSF have not approved or disapproved this manuscript, nor have passed judgment on the accuracy of the information contained herein.

REFERENCES

Bergin, M. S., D. S. Cohan, A. G. Russell, W. L. Chameides and M. T. Odman (2006). "Single-source impact analysis using 3D air quality models." *submitted to JA&WMA*.

Bergin, M. S., J. J. West, T. J. Terry J. Keating and A. G. Russell (2005). "Regional atmospheric pollution and transboundary air quality management." *Annual Review Of Environment And Resources* **30**: 1-37.

Berkowitz, C., R. Easter and S. BC (1989). "Theory and results from a quasi-steady-state precipitation-scavenging model." *Atmospheric Environment* **23**(7): 555-1571.

Boylan, J. W., M. T. Odman, J. G. Wilkinson and A. G. Russell (2006). "Integrated Assessment Modeling of Atmospheric Pollutants in the Southern Appalachian Mountains. Part II: Fine Particulate Matter and Visibility." *J. Air & Waste Manage. Assoc.* **56**: 121-122.

Boylan, J. W., M. T. Odman, J. G. Wilkinson, A. G. Russell, K. G. Doty, W. B. Norris and R. T. McNider (2002). "Development of a comprehensive, multiscale "one-atmosphere" modeling system: application to the Southern Appalachian Mountains." *Atmospheric Environment* **36**(23): 3721-3734.

Boylan, J. W., M. T. Odman, J. G. Wilkinson, A. G. Russell, K. G. Doty, W. B. Norris and R. T. McNider (2005). "Integrated assessment modeling of atmospheric pollutants in the Southern Appalachian Mountains. Part I: Hourly and seasonal ozone." *Journal of the Air & Waste Management Association* **55**(7): 1019-1030.

Boylan, J. W. and A. G. Russell (2006). "PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models." *Atmospheric Environment* **40**(26): 4946-4959.

Carter, W. P. L. (1990). "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic-Compounds." *Atmospheric Environment Part a-General Topics* **24**(3): 481-518.

Carter, W. P. L. (1995). "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic-Compounds." *Atmospheric Environment* **29**(18): 2513-2527.

Census (2002). U.S. Census Bureau. "Population Estimates". http://eire.census.gov/popest/data/states/tables/NST-EST2003-01.php (Accessed: March, 2004).

Cohan, D. S., A. Hakami, Y. Hu and A. G. Russell (2005). "Nonlinear response of ozone to emissions: Source apportionment and sensitivity analysis." *Environmental Science & Technology* **39**: 6739-6748.

Dunker, A. M. (1984). "The decoupled direct method for calculating sensitivity coefficients in chemical kinetics." *J. Chem. Phys.* **81**: 2385-2393.

Dunker, A. M., G. Yarwood, J. P. Ortmann and G. M. Wilson (2002). "The decoupled direct method for sensitivity analysis in a three-dimensional air quality model - Implementation, accuracy, and efficiency." *Environmental Science & Technology* **36**(13): 2965-2976.

EPA (Mar. 9, 2006). U.S. Environmental Protection Agency. Technology Transfer Network. " PM2.5 NAAQS Implementation". http://www.epa.gov/ttnnaaqs/pm/pm25_index.html (Accessed: Oct., 2006).

EPA (1991). Guidance for Regulatory Application of the Urban Airshed Model (UAM). . Research Triangle Park, NC.

EPA (2001). US Environmental Protection Agency, Office of Air Quality Planning & Standards, Information Transfer & Program Integration Divsion, Information Transfer Group. EPA AIRS Data. Available from: http://www.epa.gov/airsdata

EPA (2002). U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Air Trends. Available from: http://www.epa.gov/air/airtrends/highlights.html

Fine, J., L. Vuilleumier, S. Reynolds, P. Roth and N. Brown (2003). "Evaluating uncertainties in regional photochemicalair quality modeling." *Annual Review of Environment and Resources* **28**: 59-106.

Fiore, A., D. J. Jacob, H. Liu, R. M. Yantosca, T. D. Fairlie and Q. Li (2003). "Variability in surface ozone background over the United States: Implications for air quality policy." *Journal of Geophysical Research-Atmospheres* **108**(D24): 4787.

Fiore, A. M., D. J. Jacob, I. Bey, R. M. Yantosca, B. D. Field, A. C. Fusco and J. G. Wilkinson (2002). "Background ozone over the United States in summer: Origin, trend, and contribution to pollution episodes." *Journal of Geophysical Research-Atmospheres* **107**(D15).

Hakami, A., M. T. Odman and A. G. Russell (2004). "Nonlinearity in atmospheric response: A direct sensitivity analysis approach." *Journal of Geophysical Research-Atmospheres* **109**(D15).

Holloway, T., A. Fiore and M. G. Hastings (2003). "Intercontinental Transport of air pollution: Will emerging science lead to a new hemispheric treaty?" *Environmental Science & Technology* **37**(20): 4535-4542.

Kumar, N., M. T. Odman and A. G. Russell (1994). "Multiscale air quality modeling: application to southern California." *Journal of Geophysical Research* **99**(D3): 5385-5397.

Kumar, N. and A. G. Russell (1996). "Multiscale air quality modeling of the Northeastern United States." *Atmospheric Environment* **30**(7): 1099-1116.

Nenes, A., S. N. Pandis and C. Pilinis (1998). "ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols." *Aquatic Geochemistry* **4**(1): 123-152.

NPS (1995). University of CA, Davis, for the National Park Service, Air Quality Research Division. IMPROVE Data Guide: A Guide to Interpret Data. Fort Collins, CO. Available from: http://vista.cira.colostate.edu/improve/Data/IMPROVE/improve_data.htm

NRC (2004). Air Quality Management in the United States. Washington D.C., National Research Council, National Academy Press.

Odman, M. T., J. W. Boylan, J. G. Wilkinson, A. G. Russell, D. K.G., W. B. Norris, R. T. McNider, S. F. Mueller and R. E. Imhoff (2002). Southern Appalachian Mountains Initiative. SAMI Air Quality Modeling, Final Report. Asheville, NC.

Odman, M. T., J.W. Boylan, J.G. Wilkinson, A.G. Russell, S.F. Mueller, R.E. Imhoff, K.G. Doty, W.B. Norris, R.T. McNider (2002). "Integrated modeling for air quality assessment: The Southern Appalachians Mountains initiative project." *J. Phys. IV France* **12**: 211-234.

Odman, M. T. and A. G. Russell (1991). "Multiscale Modeling of Pollutant Transport and Chemistry." *Journal of Geophysical Research-Atmospheres* **96**(D4): 7363-7370.

Oreskes, N., K. Shraderfrechette and K. Belitz (1994). "Verification, Validation, and Confirmation of Numerical-Models in the Earth-Sciences." *Science* **263**(5147): 641-646.

Pandis, S. N., A. S. Wexler and J. H. Seinfeld (1993). "Secondary Organic Aerosol Formation and Transport .2. Predicting the Ambient Secondary Organic Aerosol-Size Distribution." *Atmospheric Environment Part a-General Topics* **27**(15): 2403-2416.

Pechan (2001). Pechan/Avanti Group. Southern Appalachian Mountains Initiative (SAMI) emissions projections to 2010 and 2040: growth and control data and emission estimation methodologies.

Pielke, R. A., W. R. Cotton, R. L. Walko, C. J. Tremback, W. A. Lyons, L. D. Grasso, M. E. Nicholls, M. D. Moran, D. A. Wesley and a. Lee et (1992). "A comprehensive meteorological modeling system-RAMS." *Meteorology and Atmospheric Physics* **49**(1-4): 69-91.

Russell, A. and R. Dennis (2000). "NARSTO critical review of photochemical models and modeling." *Atmospheric Environment* **34**(12-14): 2283-2324.

Russell, A. G. (2006). Personal communication.

Salmon, L. G., Cass, G.R., Pedersen, D.U., Durant, J.I., Bigg, R., Lunts, A., Utell, M. (1999). Determination of Fine Particle and Coarse Particle Concentratrations and Chemical Composition in the Northeastern United States, 1995. Available from: http://www.nescaum.org/pdf/Cass-99nescaum-pm-composition.pdf

Scott, B. (1987). Pacific Northwest Laboratory. User's Manual for the Convective Cloud Module Version 1.0. PNL-6188. Richland, WA.

Shih, J.-S., Alan Krupnick, Michelle Bergin, and Armistead Russell (2004). Resources for the Future Discussion Paper. Source-Receptor Relationships for Ozone and Fine Particulates in the Eastern United States. Washington D.C. Available from: http://ideas.repec.org/p/rff/dpaper/dp-04-25.html

Shih, J.-S., M. S. Bergin, A. Krupnick and A. G. Russell (2003). Discussion Paper 03–55, Resources For the Future. Controlling Ozone and Fine Particulates: Cost Benefit Analysis with Meteorological Variability. Washington, D.C. Available from: http://www.rff.org/Publications/Discussion_Papers.cfm

Vingarzan, R. (2004). "A review of surface ozone background levels and trends." *Atmospheric Environment* **38**(21): 3431-3442.

Wilkinson, J. G. (2006). Personal communication.

Wilkinson, J. G., C. F. Loomis, D. E. McNally, R. A. Emigh and T. W. Tesche (1994). Alpine Geophysics. Technical Formulation Document: SARMAP/LMOS Emissions Modeling System (EMS-95). AG-90/TS26 & AG-90/TS27. Pittsburgh, PA.

Yang, Y. J., J. G. Wilkinson and A. G. Russell (1997). "Fast, Direct Sensitivity Analysis of Multidimensional Photochemical Models." *Environmental Science & Technology* **31**(10).

CHAPTER 3

SINGLE-SOURCE IMPACT ANALYSIS USING 3-D AIR QUALITY MODELS

(Michelle S. Bergin, Armistead G. Russell, M. Talat Odman,
Daniel S. Cohan, and William L. Chameides.
Submitted to *the Journal of the Air & Waste Management Association*)

Implications

As state and federal agencies increasingly attempt to address ozone pollution on a regional scale, it becomes more important to understand and characterize contributions from large single sources. As part of a recent compliance enforcement action against a power plant for violation of the Clean Air Act, this study is the first to apply advanced sensitivity techniques using 3D, regional photochemical models to evaluate the impact of excess emissions from a single large source on ozone concentrations.

Abstract

The ability to evaluate the impact from a single large emissions source is becoming increasingly important for efficient air quality managment. Historically, single-source evaluations rely on short-range, linear techniques such as dispersion and receptor modeling. However, isolating the impacts of an individual source on secondary pollutants such as ozone and some components of particulate matter must incorporate non-linear processes, be sensitive to small emissions perturbations, and account for impacts that may occur hundreds of kilometers away. Here, as part of a recent compliance enforcement action for a violation of the Clean Air Act and as an evaluation of regional ozone response to single-source emissions plumes, two 3D photochemical air quality models are used to asses the impact on regional ozone from approximately 2000 to 3000 excess tons per month of NO_x emitted from a single power-plant in Ohio.

Periods in May, July, and August are evaluated. Two sensitivity methods are applied for this analysis, Brute-Force (B-F) and the Decoupled Direct Method (DDM). Using DDM, maximum one-hour averaged ozone concentrations are found to increase by 1.8, 1.3, and 2.2 ppbv during May, July, and August episodes respectively, and concentration increases greater than 0.5 ppbv occur in Ohio, Pennsylvania, Maryland, New York, West Virginia, Virginia, and North and South Carolina. B-F results were only applicable for the August episode, and predicted a maximum one-hour averaged ozone concentration increase of 2.3 ppbv. Additionally, the maximum ozone increases are compared with maximum decreases for the August period using second-order DDM, and are found, in aggregate, to be greater in magnitude by 42%. When evaluated during hours when ozone concentrations are greater than 0.060 ppm, the maximum increases in ozone are higher than decreases by 82% and the spatial extent of exacerbation is more than double that of depression.

3.1 Introduction

As our understanding of air pollution formation and interactions increases, air quality management has a greater opportunity to more effectively control pollution through programs such as emissions trading and collaborative regional planning, more effective compliance enforcement, and more specific development planning such as for a new source location or existing source expansion. Actions such as these require the ability to evaluate the impacts of a range of emissions from a single source, such as a power plant or large industrial site, on local and regional air quality. Currently, single-source evaluations generally rely on dispersion and receptor modeling, which do not account for chemical transformation or multi-day transport (EPA, 2006b). However, isolating the impacts of an individual source on secondary pollutants such as ozone and some components of particulate matter must incorporate non-linear processes and be sensitive to small emissions perturbations. Additionally, because ozone is a regional

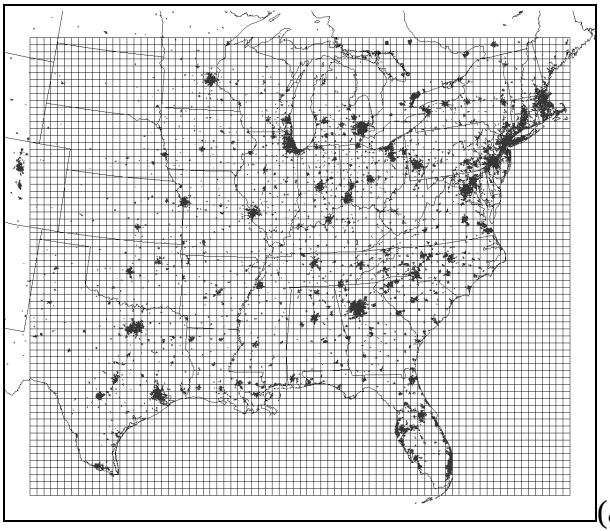
pollutant, potential impacts over a large spatial domain must be considered (Bergin *et al.*, 2005).

Physically and chemically detailed photochemical models are able to account for nonlinearities in atmospheric processes which become important under conditions such as those encountered during long-range transport, multi-day periods, and high concentration episodes. These models are typically used in regulatory or policy assessments to simulate large-scale impacts from groups or categories of sources over large spatial scales (EPA, 2006b). A "brute-force" (B-F) method is often applied for these analyses, where results from a 'baseline' air quality simulation are compared with results from an adjusted simulation which uses an altered parameter or dataset to represent the scenario of interest (e.g. reduced mobile source NO_x emissions). While the B-F method is useful for large scale perturbations, it requires significant computational resources (Yang *et al.*, 1997), and numerical errors may exceed the perturbation of the parameter if the perturbation is small, such as those from a single source. Now, recent advances in numerical techniques have allowed small perturbations to be simulated using the Decoupled Direct Method (DDM)(Dunker, 1984; Yang *et al.*, 1997). DDM calculates the derivative of a pollutant response to a perturbation, and this derivative can be linearly extrapolated to estimate a resulting pollutant concentration. However, this linear extrapolation may introduce error if there are nonlinearities in the pollutant response. To account for nonlinearity, a higher-order DDM approach has also been recently developed and implemented (Hakami, 2003; Hakami *et al.*, 2004c; Cohan *et al.*, 2005), and compares well with B-F results. While a full simulation must be run for each scenario considered using the B-F approach, first-order and higher-order DDM can account for a number of scenarios within a single simulation, reducing the computational requirements of an application.

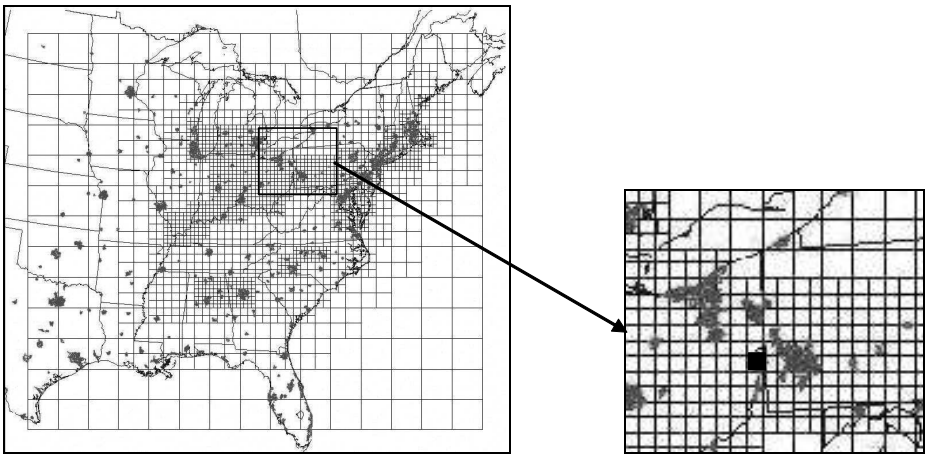
Here, a novel policy application is described which utilized DDM, higher-order DDM, and B-F in two detailed regional photochemical models for the evaluation of single-source emissions impacts in support of a recent compliance enforcement action by

the US EPA, Department of Justice, and New York, New Jersey and Connecticut for a violation of the Clean Air Act (EPA, 2006c). The lawsuit was filed in November 1999, alleging that Ohio Edison violated the New Source Review program at their W.H. Sammis Plant, a coal-fired power plant located in Stratton, Ohio near the Pennsylvania border (Figure 3.1). In August 2003, a U.S. District Court affirmed all allegations and found that Ohio Edison failed to obtain Clean Air Act (CAA) permits or to install required pollution controls for new construction projects. The modeling applications described here were performed to estimate the extent of damage caused by the excess NO_x emissions on ozone caused by the plant's failure to comply with CAA. The use of regional Eulerian models allows the evaluation to be performed over a large geographical domain. Because the exact amount of excess emissions is not well characterized, the use of B-F and of first- and second-order DDM sensitivity analysis allowed a wide range of excess emissions to be evaluated (not all scenarios evaluated are presented here).

Emissions released from coal-fired power plants are significant contributors to acid deposition, tropospheric ozone, particulate matter, and climate change, and are known to cause severe respiratory problems, damage to the immune and nervous systems, and to contribute to childhood asthma (NRC, 2004; Bergin *et al.*, 2005). These emissions include sulfur dioxides, nitrogen dioxides, and mercury and other metals. In part due to the analysis presented here, a settlement was announced in March 2005 where Ohio Edison will spend $1.1 billion between now and 2012 on various pollution controls to substantially decrease emissions at the Sammis plant and other nearby Ohio Edison power plants. Additionally, approximately 212,500 tons of SO_2 and NO_x emissions will be reduced annually, based on 2003 emissions(EPA, 2006c).



(a)



(b)

Figure 3.1. Model grids used for (a) URM-1ATM, with the location of the Sammis power plant, and (b) CMAQ simulations.

While the above case addressed quantifying damages from a facility's violation of the Clean Air Act, assessment was complicated by the fact that NO_x emissions, under certain conditions in polluted environments, can reduce ozone concentrations. Large-scale NO_x reduction, such as that required by the NO_x Budget Trading Program (e.g. the NO_x SIP call) is needed to ultimately reduce regional ozone; however, the first stages of NO_x reduction may initially decrease ozone pollution in a limited area directly downwind from the plant (Seinfeld and Pandis, 1998; Ryerson, 2001). To examine this dual

response, the Sammis plant excess emissions impacts on ozone reduction (near the plant) and exacerbation on the larger regional scale are compared. This analysis applies the higher-order DDM sensitivity method using the CMAQ model during the August simulation episode.

3.1.1 Ozone Chemistry and Power Plant Plumes

Basic scientific understanding of the processes that lead to ground-level ozone (O_3) pollution is well-established [(NARSTO, 2000) and references cited therein]. Ozone is a secondary pollutant; i.e., it is not emitted directly but is produced within the atmosphere. The production occurs via photochemical reactions involving the oxidation of volatile organic compounds (VOC) and CO in the presence of nitrogen oxides (NO_x) and sunlight. VOC, CO, and NO_x are referred to as O_3 precursors. (Since both VOC and CO play a similar role in the photochemical reactions that lead to O_3 formation, we use the term "VOC" to denote VOC and CO.) NO_x and VOC are present in the atmosphere as a result of both anthropogenic and natural emissions. Natural emissions of NO_x and VOC, along with stratospheric injection of ozone, lead to estimated natural background hourly ozone concentrations of approximately 10 to 40 ppb, while concentrations in polluted urban areas reach between 100 and 400 ppb (Seinfeld and Pandis, 1998). In the eastern half of the United States, most of the NO_x found in the lower atmosphere arises from anthropogenic emissions, while significant amounts of the VOC are natural or biogenic. The relative contributions of biogenic and anthropogenic VOC emissions depend on location and season. In relatively rural vegetated areas, during the summer when O_3 pollution is most severe, biogenic VOC emissions often dominate over anthropogenic emissions. In urban areas, anthropogenic VOC emissions often dominate over biogenic.

Air parcels exposed to intense anthropogenic emissions of NO_x generally begin in a photochemical regime where O_3 is depressed by NO-titration, and the photochemistry is

said to be VOC- or radical-limited. This situation is especially true for emissions from power plants, which are characterized by high NO_x emissions and essentially no VOC emissions. However, NO_x is oxidized in the atmosphere more rapidly than most VOCs, and VOCs from the surrounding air, often from biogenic sources, will mix into the plume. As a result, in the absence of additional anthropogenic emissions or entrainment of precursors, NO_x concentrations tend to fall more rapidly than VOCs as a plume ages, causing the ratio of VOC:NO_x to increase. As the VOC:NO_x ratio increases, NO-titration effects disappear and O_3 concentrations begin to increase in response to photochemical reactions. As the plume continues to advect and diffuse, the VOC:NO_x ratio continues to increase, and the photochemistry switches from being VOC- and radical-limited to being NO_x-limited. Photochemical generation of O_3 continues until the NO_x has been largely consumed. For these reasons, the rate and net amount of O_3 formed within a plume of pollutants that has aged significantly is often roughly proportional to the amount of NO_x added to the plume. However, NO_x emitted in a large, concentrated plume can be removed from the system through nitric acid deposition faster than NO_x emitted from more diffuse sources, resulting in less efficient O_3 production on a per-molecule basis (Ryerson, 2001). NOx may also be converted to an organonitrate (e.g. PAN or PPN), in which form it can be transported long distances before being transformed back to NO_x and subsequently producing O_3.

This theoretical expectation of how O_3 would behave within a power plant plume has been confirmed by direct field measurements [e.g., (Gillani, 1998; Ryerson, 1998; Luria, 2000; Nunnermacker, 2000; Ryerson, 2001)]. In these studies, instrumented airborne platforms (either a helicopter or airplane) were repeatedly flown through a power plant plume as it advected from its source. These experiments confirmed that NO_x emissions from power plants ultimately lead to a net increase in O_3 during the daylight hours. Along with elevating regional background ozone concentrations, O_3 concentration increases of 20 ppbv or more are commonly observed, and one case study concluded that

the second highest 1-hour averaged O_3 concentration ever measured in Atlanta (198 ppbv) was in part caused by an O_3-rich plume emanating from a nearby power plant (St. John and Chameides, 2000). This study also found that increases in NOx emissions from a single facility cause a net increase in maximum 1-hour ozone when evaluated throughout the day, and an even larger percent increase when evaluated at hours when ozone is greater than 0.060 ppm.

3.2 Method

3.2.1 Models and Input Data

To evaluate the effects of excess emissions from a power plant plume, two detailed air quality models are applied to three meteorological episodes. The excess emissions were released from the Sammis power plant between the years 1990 and 2001. Three periods during these years (referred to as 'episodes') are simulated: May 24-29, 1995, July 11-19, 1995, and August 12-20, 2000. Table 3.1 lists the tons of monthly NOx emissions estimated by the Court for each of these episodes. The emissions described are the total released and one of the likely excess emissions scenarios considered during the case hearings.

The two models applied are the Urban-to-Regional Multiscale 1-Atmosphere model (URM-1ATM) (Boylan *et al.*, 2002), and the Community Multiscale Air Quality Model (CMAQ)(Byun and Ching, 1999; NOAA/EPA, 2006). The July and May episodes are simulated using the URM-1ATM, and the August episode is simulated using CMAQ. Both of these models are three-dimensional, emissions-based photochemical Eulerian grid models. The URM-1ATM model and its predecessors have been widely used for simulating photochemical air pollutant dynamics. URM-1ATM model uses a finite element, variable mesh transport scheme with the State Air Pollution Research Center (SAPRC) chemical mechanism (Carter, 1990b; Carter, 1995) for calculating the

gas-phase reaction kinetics, and incorporates chemistry and dynamics of primary and secondary aerosols with reactive scavenging processes (Boylan *et al.*, 2002). The vertical domain has 7 non-uniform layers, with the layers thickening with an increase in altitude. Variable size grids define the horizontal domain to effectively capture the details of pollution dynamics without being computationally intensive. Emissions and meteorological input data are from a related application (Bergin *et al.*, 2006b), and were derived from a similar study performed for the Southern Appalachian Mountain Initiative (SAMI) (Boylan *et al.*, 2002; Odman, 2002b) during which the meteorological inputs were evaluated independently against National Weather Service surface observations and were found to be consistent with the current capabilities of meteorological modeling (Doty K.G., 2001). The primary difference in the application of URM-1ATM in SAMI and this application is the grid design and its resolution. Additional detail on emissions and meteorological inputs and model performance for this grid and episode are presented elsewhere (Bergin *et al.*, 2006b). Model performance was well within EPA guidelines for urban-scale modeling for both the Normalized Mean Error and the Normalized Mean Bias.

Table 3.1. NO_x emissions estimated by the Court to have been released from the Sammis power plant (tons/month).

	Total	Excess
May 1995	4295	2852
July 1995	4571	3031
August 2000	2375	1851

The CMAQ model is currently one of the most commonly utilized advanced air quality models. An evaluation of photochemical processes in CMAQ using indicators such as O_3/ NO_x, NO_z/NO_y (a measure of chemical aging), and O_3/NO_z (a measure of the O_3 production efficiency per NO_x converted), shows good agreement with the processes in the atmosphere (Arnold *et al.*, 2003). Emissions and meteorological data used for this application of CMAQ was developed as part of the Fall Line Air Quality Study (FAQS) (Chang, 2004). Meteorological inputs were evaluated and found to be accurate by air quality modeling standards (Hu *et al.*, 2003b). Performance of CMAQ in estimating ozone and PM concentrations in Georgia was superior to many prior AQM applications (Hu *et al.*, 2003a).

The grids utilized for simulations from both models cover the eastern U.S. (Figure 3.1). The CMAQ model used a uniform 36x36 km grid (Figure 3.1a). The URM model used a multiscale grid, with the finest horizontal scale being 24x24 km cells, followed by 48x48 km, 96x96 km, and 192x192 km cells (Figure 3.1b). The finest grids are placed over highly populated regions (shown by shading) such as in the Northeast corridor and over major emission source regions where many power plants and large industries are located, such as the Ohio River Valley. This scheme captures population-related emission sources such as automobile exhaust, fast food restaurants, and dry cleaners, as well as major industrial sources, and allows evaluation of potential population exposure to pollutants. Sammis is located in the shaded cell shown in the enlarged grid section (Figure 3.1b). Ozone sensitivity was also tested to emissions from the cell above Sammis, which illustrates some differences in impact due to the modeled location of emissions release.

3.2.2 Sensitivity Analysis

Sensitivity analysis is essential in determining source-receptor relationships and assessing the impacts of changing precursor emissions on ozone concentrations. Two sensitivity analysis techniques were employed here, the "brute-force" method (B-F) and the decoupled direct method (DDM) (Dunker, 1981; Dunker, 1984). The traditional B-F method involves running the model twice: first with baseline emissions and then with perturbed (increased or decreased) NO_x emissions from the plant of interest. The difference in ozone estimates of the two model simulations would be the response to the perturbed emissions. As demonstrated by Hakami et. al (Hakami *et al.*, 2004c), the B-F method is subject to increased uncertainty, especially when, as is the case here, the perturbation is small because the response is calculated as a difference between two estimates, each containing some level of numerical noise.

In DDM, sensitivity coefficients are defined as the derivatives of ozone concentration, $c[O_3]$, with respect to any given parameter (e.g. source of precursors). Here, we consider the derivative with respect to NO_x emissions from a power plant, $E[NO_x]$. The first order sensitivity coefficient, $s^{(1)}$, is then defined as

$$s^{(1)} = \frac{\partial c[O_3]}{\partial E[NO_x]} \tag{3.1}$$

and is the first derivative; $s^{(2)}$, the second-order sensitivity coefficient, is the second derivative, and so on.

Air quality models solve the atmospheric diffusion equation (ADE; equation 3.2) by calculating the change in concentration of species *i* with time,

$$\frac{\partial c_i}{\partial t} + \nabla \bullet (\mathrm{u}c_i) = \nabla \bullet (\mathrm{K}\nabla c_i) + R_i + E_i \tag{3.2}$$

where **u** is a velocity field, **K** is the diffusivity tensor, R_i represents chemical reactions of species *i* with all other species, and E_i represents emissions of species *i*. The sensitivity coefficient equations are very similar in structure to the ADE, so are subject to the same relative uncertainties as are the ozone concentrations, which are considerably less than the uncertainty obtained applying the brute force method to very small perturbations. In theory, DDM can produce reliable results for even infinitesimal changes in emissions. The DDM has been successfully applied to the first order in various air quality models including URM and CMAQ, and has been used to study air quality responses to various types of emissions (Yang *et al.*, 1997; Dunker *et al.*, 2002; Hakami *et al.*, 2004a; Bergin *et al.*, 2006b). Recently, higher order sensitivity coefficients have been used to more accurately estimate the response of non-linear systems such as ozone response to large perturbations in NO_x emissions (Hakami *et al.*, 2004c; Cohan *et al.*, 2005). The response is calculated as a Taylor series expansion:

$$\Delta c = (s\Delta E)^1 + \frac{1}{2}(s\Delta E)^2 + \ldots + \frac{1}{n!}(s\Delta E)^n \qquad (3.3)$$

where Δc is the response of the ozone concentration, ΔE is the emission perturbation, and $s^{(n)}$ is the n'th order sensitivity coefficient defined by equation 3.1.

Here, the response of ozone concentrations to a change in emissions from the Sammis plant is estimated using DDM method in two models: URM and CMAQ. DDM has been demonstrated to perform well in comparison with the brute force method for domain-wide and statewide perturbations, but here we present its application to simulating individual source effects on long-range, multi-day secondary pollution concentrations. The response estimates of the URM model consists of the first term in equation 3.3 since that model only calculates the first-order sensitivity coefficient. While

the version of CMAQ applied here calculates the first and second order sensitivity coefficients, i.e. the first and second terms in equation 3.3, Dunker et al. (Dunker *et al.*, 2002) found the first-order approximation to be very accurate up to 20% perturbations. Odman et al. (Odman *et al.*, 2002) suggested that accurate estimates of O_3 can be made by the first-order approximation for up to 30% perturbations in NO_x emissions. Hakami et al. (Hakami *et al.*, 2004c) found the second-order approximation to be very accurate up to 50% perturbations.

3.3 Results

Estimates of the maximum increase in hourly-averaged ozone concentrations per cell due to the excess NOx emissions from the Sammis plant calculated using DDM are 1.3 ppb for the July period and 2.2 ppb for the August period, both occurring in the grid-cell containing the Sammis plant from the respective models (a 24x24 km cell for July using URM, and a 36x36 km cell for August using CMAQ), and 1.8 ppb for the May period, occurring in the cell directly north of the plant (Figure 3.2). Note that the maximum increase can occur during different days and times for each cell. At other times, the same cell may exhibit a considerable decrease in ozone. As expected, the results show that meteorology strongly influences the emissions plume's pattern of spatial impact. In the July episode, maximum hourly increases larger than 0.5 ppb occur in Pennsylvania, Maryland, Ohio, and slightly in New York and West Virginia. During August, increases larger than 0.5 ppb occur in Ohio, western Pennsylvania, and in a long strip extending from the plant as far south as South Carolina. July and August are both fairly high ozone episodes, while May is a more moderate ozone episode, with increases of 0.3 ppb and greater in Ohio, Pennsylvania, and New York.

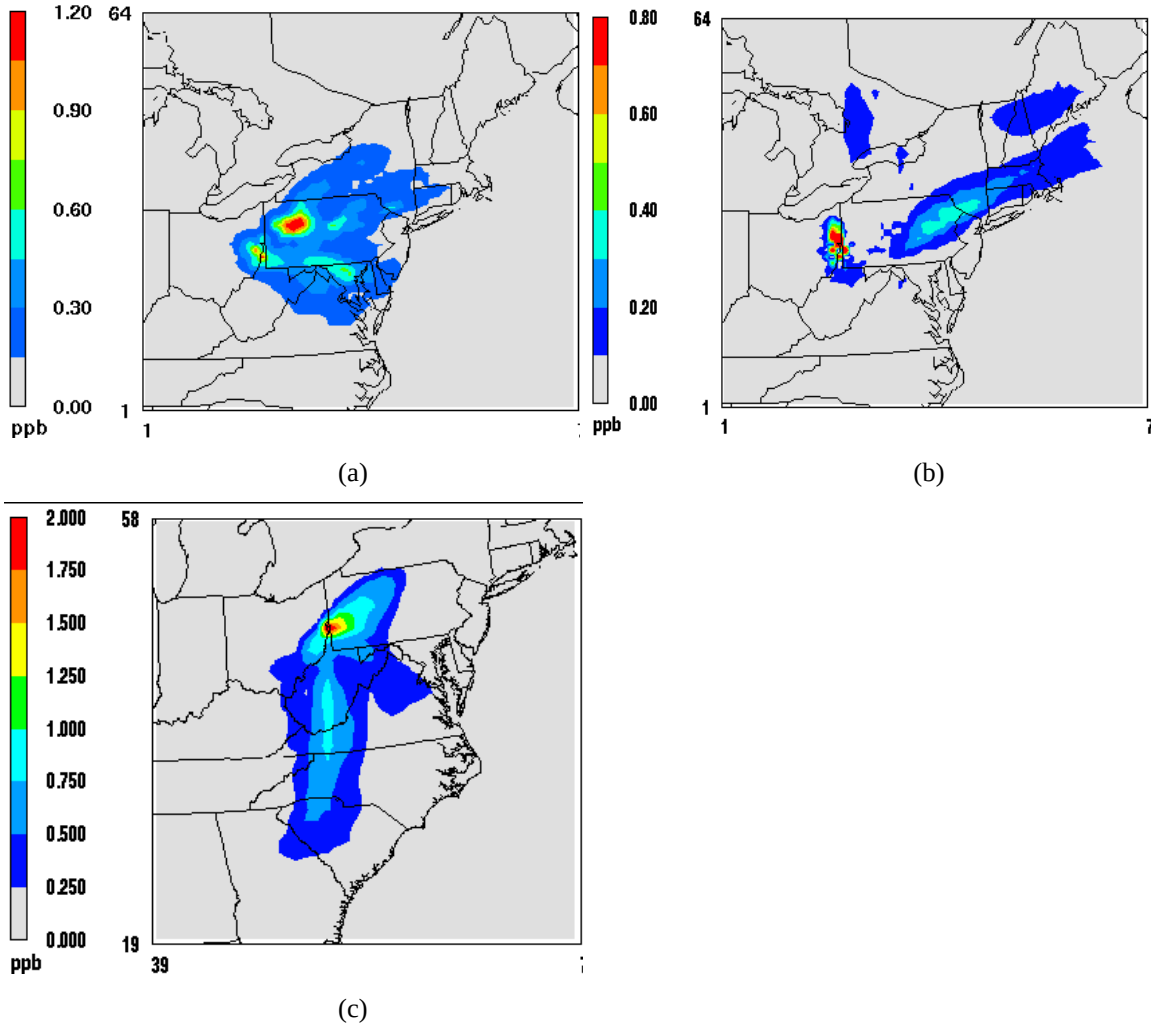
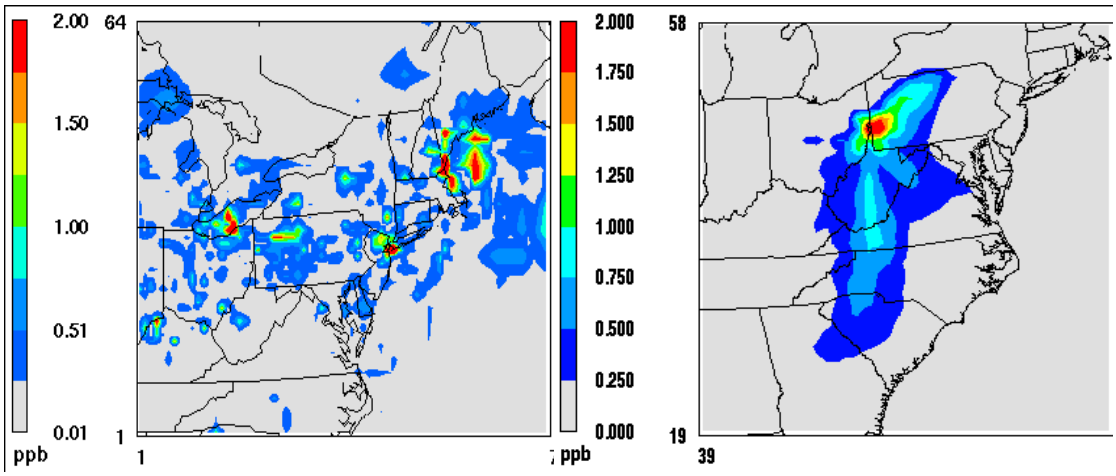


Figure 3.2 Comparison of the maximum increase in hourly-averaged ozone concentrations due to excess NO_x emissions from the Sammis plant calculated using DDM with the URM model during the periods of (a) July 11-19, 1995 and (b) May 24-29, 1995, and using (c) the CMAQ model during August 12-20, 2000.

Brute-force estimates were calculated for comparison with the DDM estimates using the URM model applied to the July episode (Figure 3.3a) and using the CMAQ model applied to the August episode (Figure 3.3b). The URM B-F application clearly demonstrates the effects of "numerical noise", which arises from trying to represent a perturbation smaller than computational errors introduced. However, the CMAQ application of the B-F method for the August episode was not overwhelmed by numerical noise. Unlike the URM application, B-F is more applicable with CMAQ because of the

uniform grid, coarser resolution, and use of different numerical methods. Results between B-F and DDM are very similar for the August episode, with a maximum increase of 2.3 ppb according to B-F and 2.2 ppb according to DDM, both peak sensitivities occurring in the grid cell containing the Sammis plant. The overall impact estimated by DDM is slightly smaller than the one estimated by the B-F method. The similarity between the B-F and DDM estimates, even though they are not independent, increases our confidence in the impact estimate.

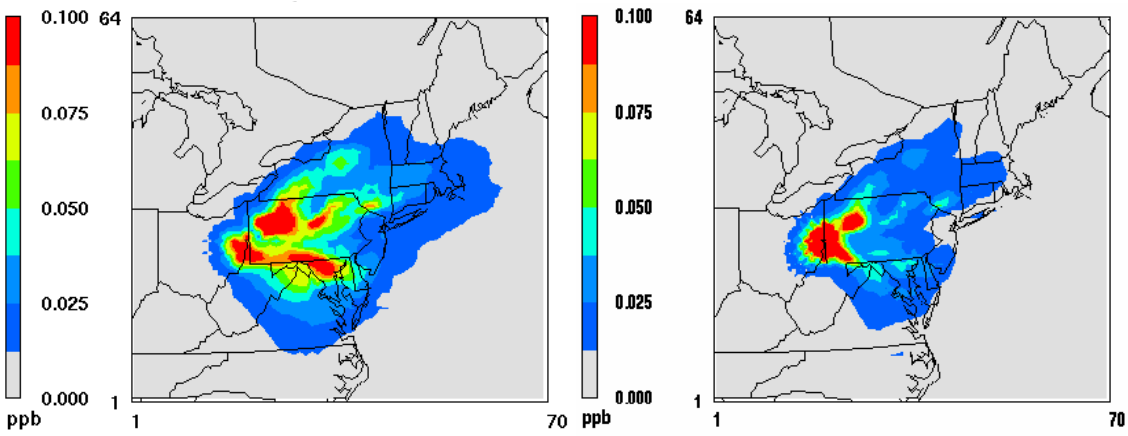


(a) (b)

Figure 3.3 Brute-force estimates of maximum increase in hourly-averaged ozone concentrations due to excess NO_x emissions from the Sammis plant using (a) the URM model applied to the July episode, and using (b) the CMAQ model applied to the August episode. The results from the URM model for July show numerical noise and are not reasonable predictions.

Besides meteorology, the location of the emission source can also be important, and differing impacts may be predicted depending on which modeling cell contains the location of the emission source. For large NO_x sources, the effects of emissions changes are highly dependant on the availability of VOC, which differs by location. For example, in the URM grid, the cell holding the Sammis plant also holds the Cardinal power plant, which emits approximately 40% more tons/day NO_x than the Sammis plant. A 10%

increase in NO_x emissions from the Sammis plant cell results in a maximum predicted ozone increase of 0.23 ppb in northwestern Pennsylvania, approximately 130 km away from the plant, with a fairly widespread spatial impact over distant states such as New York, Connecticut, Maryland and New Jersey (Figure 3.4a). If the same amount of NO_x emissions is released in one grid cell to the north, where there are no other large NO_x emissions sources, the maximum estimated ozone increase is higher, 0.81 ppb, in the emissions source cell. However, the spatial distribution of ozone impact is reduced (Figure 3.4b). A higher maximum ozone increase is expected when NO_x is emitted in the north cell because the total emissions in the cell containing the Sammis and Cardinal plants are much larger than the NO_x emissions from the north cell, and therefore require greater VOC availability to form ozone. NO_x emissions in the relatively clean cell to the north are exposed to sufficient VOC to produce ozone quickly. VOCs must be incorporated from a wider spatial area for the high concentrations of NO_x from the power-plants to complete the ozone formation cycle. These results demonstrate that even with a large difference in source cell conditions, the regional ozone impact prediction is similar in extent and magnitude.



(a) maximum = 0.23 ppb (b) maximum = 0.81 ppb

Figure 3.4. Maximum increases in hourly-averaged ozone concentrations due to a 10% increase of NO_x emissions from the Sammis plant during the July 11-19, 1995 period: (a) from its actual location collocated with the Cardinal power plant and (b) from one cell to the north.

While the above results illustrate the ozone increases caused by the excess Sammis NO_x emissions (maximum increases), excess emissions can also titrate ozone, leading to concentration reductions (maximum decreases). As with the hourly-averaged maximum increases, the maximum decrease can occur during different days and times for each cell, although the decreases largely occur at night and/or very close to the source where NO_x levels are high and VOC levels are low. When compared with Figure 3.2c, the results from the CMAQ higher-order DDM simulation of the August episode illustrate this dual response (Figure 3.5). This model and episode are used for this analysis because they offer the most confidence due to the B-F agreement with DDM. Maximum decreases in hourly ozone concentrations are found to be of a similar order of magnitude, covering a more local area (Figure 3.5). In aggregate, ozone increases are 42% larger in magnitude than the decreases (Table 3.2). Additionally, when evaluated over hours when ozone concentrations are greater than 0.060 ppm (mostly during daylight and downwind of high emissions), ozone maximum increases are 82% larger and cover almost double the area than maximum decreases (Figure 3.6, Table 3.2).

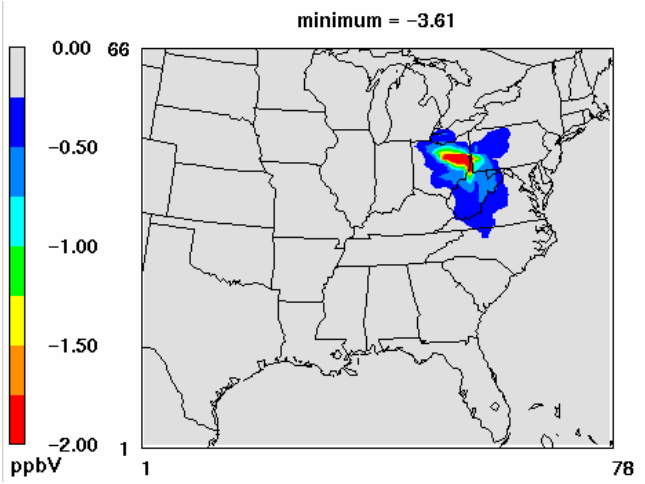
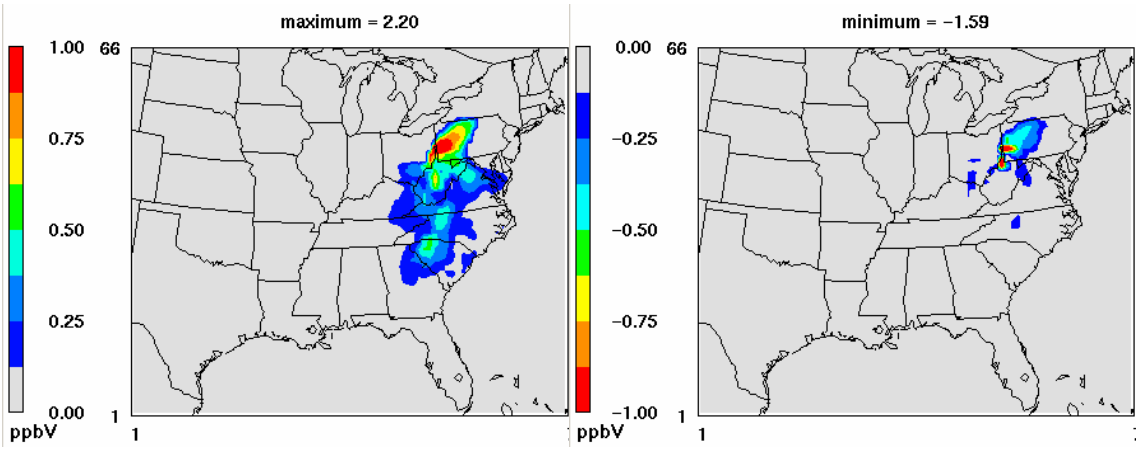


Figure 3.5. Maximum decreases in hourly-averaged ozone concentrations due to excess emissions from the Sammis power plant during the August episode.



(a) (b)

Figure 3.6. Maximum (a) increases and (b) decreases in hourly-averaged ozone concentrations per model cell due to excess emissions from the Sammis power plant during the August episode when ozone concentrations are greater than 0.060 ppm.

Table 3.2. Sum of model cell hourly maximum increases and decreases in ozone concentration accounting for first and second order sensitivity response to excess NO_x emissions from the Sammis plant during the August episode, summed over all hours and over hours when ozone is greater than 0.060 ppm.

Hours	Ozone Decreases (ppb)	Ozone Increases (ppb)	*Percent difference (%)
All	29,659	50,974	41.8
When O_3 > 0.060 ppm	7,708	42,392	81.8

* Percent difference = 100% * (increase - decrease)/increase

While the use of three-dimensional Eulerian models with direct sensitivity analysis allows evaluation of a range of emissions scenarios over a large spatial domain, some limitations necessarily exist in this approach when applied to evaluation of single sources. In particular, the power-plant emission plume is immediately diffused throughout the cell containing the plant location. Ozone chemistry is dependent on surrounding conditions, and the NO_x and O_3 concentration diffusion may affect the

predicted ozone peak and spatial distribution. Smaller model cells may reduce this error, and comparison with predictions from a 'plume-in-grid' model (i.e. a model that treats emissions plumes on a sub-grid scale) would be useful.

3.4 Conclusions

Results presented here demonstrate the use of 3D photochemical air quality models using first and second order DDM and B-F for nonlinear, long-range evaluation of single-source emissions impacts for use in regional air quality management applications. This analysis supported a recent compliance enforcement action by the US EPA, Department of Justice, and several states for a violation of the Clean Air Act (EPA, 2006c). Excess NO_x emissions from the Sammis power-plant in Stratton, Ohio are predicted to have increased maximum one-hour averaged ozone concentrations over a large region, including increases greater than 0.5 ppbv in Ohio, Pennsylvania, Maryland, New York, West Virginia, Virginia, and North and South Carolina. Simulated peak maximum one-hour averaged concentrations are found to have increased up to 2.3 ppbv. Additionally, the excess emissions from the Sammis plant are shown to cause some reductions in maximum hourly ozone concentrations. However, when evaluated over all hours and only during hours of elevated ozone concentrations (greater than 0.060 ppm), the aggregate increases are greater than the decreases.

While these calculated ozone sensitivities are low, the spatial distributions are large, and cumulative impacts from single-sources are high and increasing worldwide (Fiore *et al.*, 2002a; Fiore *et al.*, 2003). It is important to develop techniques to characterize contributions to pollutants from large individual sources in order to design and enforce air quality control strategies. While influenced by uncertainties, model assessments such as this one, in conjunction with ambient measurements and controlled experiments, are the only methods available for predicting and learning about the dynamic and integrated system of emissions and secondary pollutants, and provide useful

guidance for the design of efficient air quality control programs. An application comparison with currently available plume-in-grid models would be beneficial to both plume-in-grid model development as well as for analysis of the effects of plume dispersion in the Eulerian models used here.

Acknowledgments

The research presented was largely performed in support of Civil Action No. C2-99-1181, UNITED STATES et al v. OHIO EDISON et al, and as such was funded by the U.S. Department of Justice. In addition, M. T. Odman and W. L. Chameides were expert witnesses for this case on behalf of the plaintiffs. Partial funding was also provided under US EPA grants RD82897602, RD83107601, and RD83096001. The opinions, findings, conclusions, and recommendations are those of the authors and do not necessarily represent the views of the DOJ or EPA. The DOJ and EPA have not approved or disapproved this manuscript, nor have passed judgment on the accuracy of the information contained herein.

REFERENCES

Arnold, J. R., R. L. Dennis and G. S. Tonnesen (2003). "Diagnostic evaluation of numerical air quality models with specialized ambient observations: testing the Community Multiscale Air Quality modeling system (CMAQ) at selected SOS 95 ground sites." *Atmosperic Environment* **37**(9-10): 1185-1198.

Bergin, M. S., J.-S. Shih, A. J. Krupnick, J. W. Boylan, J. G. Wilkinson, M. T. Odman and A. G. Russell (2006). "Regional Air Quality: Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States." *Submitted to Environ. Sci. & Technol*.

Bergin, M. S., J. J. West, T. J. Terry J. Keating and A. G. Russell (2005). "Regional atmospheric pollution and transboundary air quality management." *Annual Review of Environment And Resources* **30**: 1-37.

Boylan, J. W., M. T. Odman, J. G. Wilkinson, A. G. Russell, K. G. Doty, W. B. Norris and R. T. McNider (2002). "Development of a comprehensive, multiscale "one-atmosphere" modeling system: application to the Southern Appalachian Mountains." *Atmospheric Environment* **36**(23): 3721-3734.

Byun, D. W. and J. K. S. Ching (1999). U.S. Environmental Protection Agency, Office of Research and Development. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. . Washington, D.C.

Carter, W. P. L. (1990). "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic-Compounds." *Atmospheric Environment Part a-General Topics* **24**(3): 481-518.

Carter, W. P. L. (1995). "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic-Compounds." *Atmospheric Environment* **29**(18): 2513-2527.

Chang, M. E., Russell, A.G., Baumann , K., et al. (2004). Georgia Institute of Technology. The Fall-line Air Quality Study (FAQS): Draft Final Report. Atlanta, GA. Available from: http://cure.eas.gatech.edu/faqs/finalreport/.

Cohan, D. S., A. Hakami, Y. Hu and A. G. Russell (2005). "Nonlinear response of ozone to emissions: Source apportionment and sensitivity analysis." *Environmental Science & Technology* **39**: 6739-6748.

Doty K.G., T. T. W., McNally D.E, Timin B. and Mueller S.F. (2001). Meteorological Modeling for the Southern Appalachian Mountains Initiative (SAMI). Final Report, Southern Appalachian Mountain Initiative. Asheville, N.C.

Dunker, A. M. (1981). "Calculation of sensitivity coefficients for complex atmospheric models." *Atmos. Environ.* **15**: 1155-1161.

Dunker, A. M. (1984). "The decoupled direct method for calculating sensitivity coefficients in chemical kinetics." *J. Chem. Phys.* **81**: 2385-2393.

Dunker, A. M., G. Yarwood, J. P. Ortmann and G. M. Wilson (2002). "The decoupled direct method for sensitivity analysis in a three-dimensional air quality model - Implementation, accuracy, and efficiency." *Environmental Science & Technology* **36**(13): 2965-2976.

EPA (2006a). U.S. Environmental Protection Agency. Support Center for Regulatory Atmospheric Modeling. "Air Quality Models". http://www.epa.gov/scram001/aqmindex.htm (Accessed: Feb., 2006).

EPA (2006b). "Ohio Edison Company, W.H. Sammis Power Station, Clean Air Act Settlement". http://www.epa.gov/compliance/resources/cases/civil/caa/ohioedison.html (Accessed: Feb., 2006).

Fiore, A., D. J. Jacob, H. Liu, R. M. Yantosca, T. D. Fairlie and Q. Li (2003). "Variability in surface ozone background over the United States: Implications for air quality policy." *Journal of Geophysical Research-Atmospheres* **108**(D24): 4787.

Fiore, A. M., D. J. Jacob, I. Bey, R. M. Yantosca, B. D. Field, A. C. Fusco and J. G. Wilkinson (2002). "Background ozone over the United States in summer: Origin, trend, and contribution to pollution episodes." *Journal of Geophysical Research-Atmospheres* **107**(D15).

Gillani, N. V., J.F. Meagher, R.V. Valente, R.E. Imhoff, and R.L. Tanner (1998). "Relative production of ozone and nitrates in urban and rural power plant plumes

I. Comparative results based on data from 10 field measurement days." *J. Geophys. Res.* **103**: 22593- 22617.

Hakami, A., M. S. Bergin and A. G. Russell (2004a). "Ozone formation potential of organic compounds in the eastern United States: A comparison of episodes, inventories, and domains." *Environmental Science & Technology* **38**(24): 6748-6759.

Hakami, A., Bergin, M. S., Russell, A. G. (2003). Report to the American Chemistry Council and California Air resources Board. Assessment of the ozone and aerosol formation potentials (reactivities) of organic compounds over the eastern United States.

Hakami, A., M. T. Odman and A. G. Russell (2004b). "Nonlinearity in atmospheric response: A direct sensitivity analysis approach." *Journal of Geophysical Research-Atmospheres* **109**(D15).

Hu, Y.-T., M. T. Odman and A. G. Russell (2003a). Georgia Department of Natural Resources. Air Quality Modeling of the First Basecase Episode for the Fall Line Air Quality Study. Draft final report. Atlanta, GA.

Hu, Y.-T., M. T. Odman and A. G. Russell (2003b). Georgia Department of Natural Resources. Meteorological Modeling of the First Basecase Episode for the Fall Line Air Quality Study. Final report. Atlanta, GA.

Kumar, N., M. T. Odman and A. G. Russell (1994). "Multiscale air quality modeling: application to southern California." *Journal of Geophysical Research* **99**(D3): 5385-5397.

Kumar, N. and A. G. Russell (1996). "Multiscale air quality modeling of the Northeastern United States." *Atmospheric Environment* **30**(7): 1099-1116.

Luria, M., R.L. Tanner, R.E. Imhoff, R.J. Valente, E.M. Bailey, and S.F. Mueller (2000). "Influence of natural hydrocarbons on ozone formation in an isolated power plant plume." *J. Geophys. Res.* **105**: 9177-9188.

NARSTO (2000). North American Research Strategy on Tropospheric Ozone. Published by the Electric Power Research Institute. An Assessment of Tropospheric Ozone - A North American Perspective.

NOAA/EPA. "The Community Multiscale Air Quality model (CMAQ)." http://www.epa.gov/asmdnerl/CMAQ/cmaq_model.html (Accessed Feb., 2006).

NRC (2004). Air Quality Management in the United States. Washington D.C., National Research Council, National Academy Press.

Nunnermacker, L. J., L.I. Kleinman, D. Imre, P.H. Daum, Y. –N. Lee, J.H. Lee, S. R. Springston, and L. Newman (2000). "NOy lifetimes and O3 production efficiencies in urban and power plant plumes: Analysis of field data." *J. Geophys. Res.* **105**: 9165-9176.

Odman, M. T., J. W. Boylan, J. G. Wilkinson, A. G. Russell, D. K.G., W. B. Norris, R. T. McNider, S. F. Mueller and R. E. Imhoff (2002). Southern Appalachian Mountains Initiative. SAMI Air Quality Modeling, Final Report. Asheville, NC.

Odman, M. T., J.W. Boylan, J.G. Wilkinson, A.G. Russell, S.F. Mueller, R.E. Imhoff, K.G. Doty, W.B. Norris, R.T. McNider (2002). "Integrated modeling for air quality assessment: The Southern Appalachians Mountains initiative project." *J. Phys. IV France* **12**: 211-234.

Odman, M. T. and A. G. Russell (1991). "Multiscale Modeling of Pollutant Transport and Chemistry." *Journal of Geophysical Research-Atmospheres* **96**(D4): 7363-7370.

Ryerson, T. B., M. Trainer, J.S. Holloway, D.D. Parrish, L.G. Huey, D.T. Sueper, G.J. Frost, S.G. Donnelly, S. Schauffler, E.L. Atlas, W.C. Kuster, P.D. Goldan, G. Hubler, J.F. Meagher, F.C. Fehsenfeld (2001). "Observations of ozone formation in power plant plumes and implications for ozone control strategies." *Science* **292**: 719-723.

Ryerson, T. B., M.P. Buhr, G.J. Frost, P.D. Goldan, J.S. Holloway, G. Hubler, B.T. Jobson, W.C. Kuster, S.A. McKeen, D.D. Parrish, J.M. Roberts, D.T. Sueper, M. Trianer, J. Williams, and F.C. Fehsenfeld (1998). "Emissions lifetimes and ozone formation in power plant plumes." *J. Geophys. Res.* **103**: 22569-22583.

Seinfeld, J. H. and S. N. Pandis (1998). Atmospheric Chemistry and Physics. New York, NY, Wiley.

St. John, J. C. and W. L. Chameides (2000). "Possible role of power plant emissions in fostering O3 exceesance events in Atlanta, Georgia." *J. Geophys. Res.* **105**: 9203-9211.

Yang, Y. J., J. G. Wilkinson and A. G. Russell (1997). "Fast, Direct Sensitivity Analysis of Multidimensional Photochemical Models." *Environmental Science & Technology* **31**(10).

CHAPTER 4

VOLATILE ORGANIC COMPOUNDS AND COOPERATIVE POLICY DEVELOPMENT AND SUPPORT

4.1 Introduction

This thesis chapter consists of two main sections, each addressing emissions of volatile organic compounds (VOCs) and their impacts on air quality, and illustrating cooperative participation between technical, regulatory, and regulated communities for the design of efficient regulatory solutions. The first section, 4.2, Organic Solvent Impacts on Tropospheric Air Pollution, is published in the Handbook of Solvents. Solvent utilization is as the single largest VOC emissions source listed in the EPA National Emissions Inventory (NEI) Air Pollutant Emissions Trends Data for the year 2002 (EPA, 2005a), slightly above highway vehicles, and this estimate does not include emissions related to the manufacture, storage, or transport of these chemicals. Solvents contribute to tropospheric ozone, exposure to toxic compounds, stratospheric ozone depletion, the accumulation of Persistent Organic Pollutants (POPs) (E-PRTR, 2006), and to secondary organic aerosols (although the extent of which is currently uncertain)(Bergin and Russell, 2001).

The solvent industry is subject to a wide variety of environmentally protective regulations, and as such has significant incentives to participate in the design of policy that allows for flexibility to accommodate low-cost options for compliance. An important purpose of this section is to provide information to solvent producers and users about the impacts of their activities on air quality. When opportunities arise for process changes, reformulation, or other actions that could alter use patterns or composition or rates of emissions of organic solvents, they then have some ability to select lower impact options than may have otherwise occurred. Similarly to the discussion in “Achieving

Successful Regimes for Transboundary Air Pollution" in Chapter 5, policy and regulatory actions are most successful when all parties affected by the regulations participate in the policy development process from an early stage, acting from an informed position. Communications between the scientific and regulated communities can build trust, a common understanding of the issues and positions, and increased technical capacity within the regulated community which can all help make the regulatory system more efficient through increased consensus, cooperation, and valuable input and feedback.

The publication of the Handbook section was, in large part, the result of the solvent industries' interest in air quality issues due to the contributions of volatile organic solvents to the formation of tropospheric ozone. The history of regulatory control of VOC emissions in the United States as part of an attempt to control tropospheric ozone demonstrates the dynamic, iterative relationships between science, policy, and the regulated communities, as well as the potential for both failure and success in pollution control strategies. The second main section of this thesis chapter, 4.3, Regulatory Applications Accounting for the Ozone Formation Potential of Volatile Organic Compounds, presents some scientific challenges and solutions as scientists, policy makers, and industry representatives collaborated to design regulations accounting for the differences in ozone formation potential, or 'reactivity', of volatile organic compounds.

The main scientific barriers to accounting for reactivity in regulations were identifying important VOCs, quantification of their reactivity, and evaluating and accounting for uncertainty and variability in the quantification measures. VOC reactivity is a function of the chemical and meteorological atmosphere it is emitted into, as well as a function of the compound properties. Hundreds of different compounds are VOCs and are emitted by an extensive variety of sources, the full environmental impacts of which are unknown. An ideal regulatory design would protect air quality while incorporating flexibility for individual sources to tailor emissions control methods to their particular situation, at the same time providing incentives for developing an improved emissions

inventory to aid in identifying the effects of these compounds on health and the environment.

As described below, progress in this research topic has resulted in four regulatory applications to date, and because of recent encouragement by the US EPA and research results supporting the use of reactivity measures on regional scales, more applications are expected in the near future. The evolution and success of this air quality control strategy highlights the importance of participation by all impacted parties, incorporation of feedback, and continuing scientific research for development of effective pollution control policy.

4.2 Organic Solvent Impacts on Tropospheric Air Pollution

Michelle Bergin and Armistead Russell. Chapter 17(4), 1188-1200. In Handbook of Solvents (Wypych, G. Ed.) ChemTec Publishing, Toronto, CA. (2001)

4.2.1 Sources and Impacts of Volatile Solvents

Solvents, either by design or default, are often emitted into the air, and the total mass of emissions of solvents is not small. In a typical city in the United States, solvents can rival automobile exhaust as the largest source category of volatilized organic compound (VOC) emissions into the atmosphere(SCAQMD, 1997). In the United Kingdom, solvent usage accounted for 36% of the estimated total VOC mass emissions in 1995 (Derwent and Pearson, 1997). Such widespread emissions lead to increased concentrations of many different compounds in the ambient environment, and their release has diverse impacts on air quality.

A large variety of solvent-associated compounds are emitted, many of which are hydrocarbons, oxygenates. Those solvents may have multiple atmospheric impacts. For example, toluene is potentially toxic and can reach relatively high concentrations at small spatial scales, such as in a workplace. Toluene also contributes to the formation of

tropospheric ozone at urban scales, while at regional scales toluene can lower the rate of tropospheric ozone formation. Other solvents likewise can have a range of impacts, ranging from local contamination to modification of the global climate system.

This diversity of potential impacts is due, in part, to differences in the chemical properties and reactions that a compound may undergo in the atmosphere, differences in emissions patterns, and differences in the spatial and temporal scales of atmospheric phenomena. Transport and fate of chemical species is closely tied to the speed at which the compound degrades (from seconds to centuries, depending on the compound) as well as to the environmental conditions in which the compound is emitted. If a compound degrades very quickly, it may still have toxic effects near a source where concentrations can be high. In contrast, extremely stable compounds (such as chlorofuorocarbons: CFCs) are able to circumvent the globe, gradually accumulating to non-negligible concentrations (IPCC, 1996).

Of the myriad of solvents emitted into the air, the ones of primary concern are those with the greatest emissions rates, and/or those to which the environment has a high sensitivity. Compounds with very large emissions rates include tri- and tetrachloroethylene (e.g., from dry-cleaning), aromatics (benzene, toluene and xylenes, e.g., from coatings), alcohols, acetone and, historically, CFCs. While those compounds are often emitted from solvent use, other applications lead to their emission as well. For example, gasoline is rich in aromatics and alkanes, and in many cases fuel use dominates emissions of those compounds. CFCs have been used as refrigerants and as blowing agents. This diversity of originating sources makes identifying the relative contribution of solvents to air quality somewhat difficult since there are large uncertainties in our ability to quantify emissions rates from various source categories.

Solvents with a high environmental sensitivity include benzene (a potent carcinogen), xylenes (which are very effective at producing ozone), formaldehyde (both toxic and a strong ozone precursor), and CFCs (ozone depleters and potential greenhouse

gases). Most of the solvents of concern in terms of impacting ambient air are organic, either hydrocarbons, oxygenated organics (e.g., ethers, alcohols and ketones) or halogenated organics (e.g•, dichlorobenzene). Some roles of these compounds in the atmosphere are discussed below.

While the toxicity of some solvents is uncertain, the role of emissions on direct exposure is not in question. Indoors, vaporized solvents can accumulate to levels of concern for acute and/or chronic exposure. However, the toxicity of solvents outdoors is not typically of as great of concern as indoors except very near sources. Outdoors, solvents have adverse effects other than toxicity. The importance of CFC emissions on stratospheric ozone, for example, is significant, but the problem is well understood and measures are in place to alleviate the problem. Reactive compounds can also aid in the formation of other pollutants, referred to as secondary pollutants because they are not emitted, but formed from directly emitted primary precursors. Of particular concern is tropospheric ozone, a primary constituent of photochemical smog. In the remainder of this chapter, the impacts of solvents on air quality are discussed, with particular attention given to the formation of tropospheric ozone. This emphasis is motivated by current regulatory importance as well as by lingering scientific issues regarding the role of volatile organics in secondary pollution formation.

4.2.2 Modes and Scales of Impact

Many organic solvents are toxic, and direct exposure to the compound through the atmosphere (e.g., via inhalation) can be harmful. While toxic effects of solvents rely on direct exposure, many solvents also contribute to the formation of secondary pollutants such as tropospheric ozone or particulate matter (PM), which cause health problems and damage the environment on larger spatial scales such as over urban areas and multi-state/country regions. Very slowly reacting solvent compounds also impact the atmosphere on the global scale, which may cause imbalances in living systems and in the

environment. While some mechanisms of environmental imbalance are understood, the risks associated with global atmospheric impacts are highly uncertain.

Transport of solvents in the atmosphere is similar to most other gaseous pollutants, and is dominated by the wind and turbulent diffusion. There is little difference between the transport of different solvent compounds, and the fact that most solvents have much higher molecular weights than air does not lead to enhanced levels at the ground. Heavy solvents are, for the most part, as readily diffused as lighter solvents, although they may not vaporize as fast. The higher levels of many solvents measured near the ground are due to proximity to emissions sources, which are near the surface, and the fact that most solvents degrade chemically as they mix upwards. A major difference in the evolution of various solvents is how fast they react chemically. Some, such as formaldehyde, have very short lifetimes while others, such as CFCs, last decades.

4.2.2.1 Direct exposure

Volatilization of solvents allows air to serve as a mode of direct exposure to many compounds known to be toxic. Generally, direct exposure is a risk near strong or contained sources, and can cause both acute and chronic responses. Most of the non-workplace exposure to solvents occurs indoors. This is not surprising since, on average, people spend a vast majority of their time indoors, and solvents are often used indoors. Outdoors, solvents rapidly disperse and can oxidize, leading to markedly lower levels than what is found indoors near a source. For example, indoor formaldehyde levels are often orders of magnitude greater than outdoors. There still are cases when outdoor exposure may be non-negligible, such as if one spends a significant amount of time near a major source. Toxic effects of solvents are fairly well understood, and many countries have developed regulatory structures to protect people from direct exposure. The toxic effects of solvent emissions on ecosystems are less well understood, but are of growing concern.

4.2.2.2 Formation of secondary compounds

In addition to transport, organic compounds emitted into the air may also participate in complex sets of chemical reactions. While many of these reactions "cleanse" the atmosphere (most organic compounds ultimately react to form carbon dioxide), a number of undesirable side effects may also occur. Such adverse impacts include the formation of respiratory irritants and the destruction of protective components of the atmosphere. Ozone is a classic example of the complexity of secondary atmospheric impacts. Ozone is a highly reactive molecule consisting of three oxygen atoms (O_3). In one part of the atmosphere ozone is beneficial, in another it is a pollutant of major concern. Solvents and other organic emissions may either increase or decrease ozone concentrations, depending on the compound, location of reaction, and background chemistry. The mechanisms of some adverse secondary responses are discussed below.

4.2.2.3 Spatial scales of secondary effects

Two layers of the Earth's atmosphere are known to be adversely impacted by solvents - the troposphere and the stratosphere. These two layers are closest to Earth, and have distinct chemical and physical properties. The troposphere (our breathable atmosphere) is the closest layer, extending from the Earth to a height of between 10 to 15 km. The rate of chemical reaction generally determines the spatial scale over which emissions have an impact in the troposphere. Most non-halogenated solvents have lifetimes of a week or less, and elevated concentrations will only be found near the sources (NRC, 1991). Compounds that do not react rapidly in the troposphere (e.g., CFCs) are relatively uniformly distributed, and may eventually reach the stratosphere.

The stratosphere is the next vertical layer of the atmosphere, extending from the tropopause (the top of the troposphere) to about 50 km in altitude. Little vertical mixing occurs in the stratosphere, and mixing between the troposphere and the stratosphere is

slow. Impacts on the stratosphere can be considered global in scale, while impacts on the troposphere are generally urban or regional in scale. Distinct chemical systems of interest concerning solvents in the atmosphere are stratospheric ozone depletion, global climate change, and tropospheric photochemistry leading to enhanced production of ozone, particulate matter, and other secondary pollutants such as organonitrates.

4.2.2.3.1 Global Impacts

Because some solvent compounds are nearly inert, they can eventually reach the stratosphere where they participate in global scale atmospheric dynamics such as the destruction of stratospheric ozone and unnatural forcing of the climate system. Stratospheric ozone depletion by chlorofuorocarbons (CFCs) is a well-known example of global scale impacts. CFCs were initially viewed as environmentally superior to organic solvents. They are generally less toxic than other similarly acting compounds, less flammable and are virtually inert in the troposphere. Replacing solvents using volatile organic compounds (VOCs) with CFCs was hoped to reduce the formation of tropospheric ozone and other secondary pollutants. Because of their inert properties, there are no effective routes for the troposphere to remove CFCs, and, over the decades, emissions of CFCs have caused their accumulation, enabling them to slowly leak into the stratosphere. In the stratosphere, the strong ultraviolet (UV) light photodissociates CFCs, releasing chlorine, which then catalytically attacks ozone. CFC use has been largely eliminated for that reason. Partially halogenated organic solvents do not contribute as seriously to this problem since they react faster in the troposphere than CFCs, so the associated chlorine does not reach the stratosphere as efficiently. CFCs and other solvent compounds also have a potential impact on global climate change.

4.2.2.3.2 Stratospheric Ozone Depletion

Natural concentrations of stratospheric O_3 are balanced by the production of ozone via photolysis of oxygen by strong UV light, and destruction by a number of pathways, including reactions with nitrogen oxides and oxidized hydrogen products that are present. Photolysis of an oxygen molecule leads to the production of two free oxygen atoms:

$$O_2 + hv \rightarrow O + O \quad (4.1)$$

Each oxygen atom can then combine with an oxygen molecule to form ozone:

$$O + O_2 \rightarrow O_3 \quad (4.2)$$

Ozone is then destroyed when it reacts with some other compound, e.g., with NO:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (4.3)$$

Addition of either chlorine or bromine atoms leads to extra, and very efficient, pathways for ozone destruction. The free chlorine (or bromine) atom reacts with ozone, and the product of that reaction removes a free oxygen atom:

$$Cl + O_3 \rightarrow ClO + O_2 \quad (4.4)$$

$$\underline{ClO + O \rightarrow Cl + O_2} \quad (4.5)$$

Net (reactions 4.2.4 +4.2.5 together): $O_3 + O \rightarrow 2\ O_2$ (4.6)

Removing a free oxygen atoms also reduce ozone since one less ozone molecule will be formed via reaction 4.2. Thus, the chlorine atom reactions effectively remove two ozone molecules by destroying one and preventing the formation of another. Additionally, the original chlorine atom is regenerated to catalytically destroy more ozone. This reaction cycle can proceed thousands of times, destroying up to 100,000 molecules of O_3 before the chlorine is removed from the system (e.g., by the formation of HCl).

Reduction of ozone is greatly enhanced over the poles by a combination of extremely low temperatures, decreased transport and mixing, and the presence of polar stratospheric clouds that provide heterogeneous chemical pathways for the regeneration of atomic chlorine: The resulting rate of O_3 destruction is much greater than the rate at which it can be naturally replenished.

Current elevated levels of CFCs in the troposphere will provide a source of chlorine to the stratosphere for decades, such that the recent actions taken to reduce CFC emissions (through the Montreal Protocol) will have a delayed impact.

4.2.2.3.3 Global Climate Forcing

Over the past decade, the potential for non-negligible changes in climate caused by human activity has been an issue of great concern. Very large uncertainties are associated with both estimations of possible effects on climate as well as estimations of the potential impacts of changes in climate. However, current consensus in the international scientific community is that observations suggest "a discernible human influence on global climate" (IPCC, 1996).

Solvent compounds, especially CFCs and their replacements, participate in climate change as "greenhouse gases". Greenhouse gases allow short-wave solar radiation to pass through, much of which the earth absorbs and re-radiates as long-wave radiation. Greenhouse gases absorb the long-wave radiation, causing the atmosphere to heat up, thereby acting as a blanket to trap radiation that would normally vent back to space. Climate change is a controversial and complex issue, but it is likely that restrictions such as those from the Kyoto Protocol will be adopted for emissions of compounds strongly suspected of exacerbating climate change. Many countries have already adopted stringent policies to reduce greenhouse gas emissions.

4.2.2.3.4 Urban and regional scales

Another area of concern regarding outdoor air is exposure to secondary pollutants that are, in part, due to chemical reactions involving solvent compounds. Examples include the formation of elevated levels of ozone, formaldehyde, organonitrates, and particulate matter. Formaldehyde, a suspected carcinogen, is an oxidation product of organic compounds. Tropospheric ozone and organonitrates, as discussed below, are formed from a series of reactions of organic gases and nitrogen oxides in the presence of sunlight. Particulate matter formation is linked to ozone, and some solvents may react to form particulate matter. The particulate matter of greatest current concern is small (generally less than 2.5 µm in diameter) and is usually formed by gas-to-aerosol condensation of compounds via atmospheric chemical reactions. Ozone and particulate matter are both regulated as "criteria" pollutants in the United States because they have been identified as risks to human health. Ozone is believed to cause respiratory problems and trigger asthma attacks, and PM has a variety of suspected adverse health outcomes (e.g., respiratory and coronary stress and failure). Many organonitrates, such as peroxyacetyl nitrate, are eye irritants and phytotoxins. Currently, the formation and effects of ozone are better understood than those of fine particulate matter and organonitrates. The following section of this chapter discusses the effects, formation, and control of tropospheric ozone. The role of solvents in forming particulate matter is currently viewed as less urgent.

4.2.3 Tropospheric Ozone

Tropospheric ozone, a primary constituent of photochemical smog, is naturally present at concentrations on the order of 20-40 parts per billion (ppb) (NRC, 1991). However, elevated levels of ground-level ozone are now found virtually worldwide, reaching in some cities concentrations of up to 10 times the natural background.

4.2.3.1 Effects

Ozone is believed to be responsible for both acute (short-term) and chronic (long-term) impacts on human health, especially on lung functions. Major acute effects of ozone are decreased lung function and increased susceptibility to respiratory problems such as asthma attacks and pulmonary infection. Short-term exposure can also cause eye irritation, coughing, and breathing discomfort (OTA, 1989; Lippmann, 1991; Horvath and McKee, 1994). Evidence of acute effects of ozone is believed to be "clear and compelling" (Lippmann, 1993). Chronic health effects may present a potentially far more serious problem; however, definitive evidence is difficult to obtain. Recent studies do suggest that ambient levels of ozone induce inflammation in human lungs, which is generally accepted as a precursor to irreversible lung damage, (Horvath and McKee, 1994) and chronic animal exposure studies at concentrations within current ambient peak levels indicate progressive and persistent lung function and structural abnormalities.(OTA, 1989; Lippmann, 1993)

Crop damage caused by air pollution has also received much attention. It is estimated that 10% to 35% of the world's grain production occurs in regions where ozone pollution likely reduces crop yields (Chameides *et al.*, 1994). Air pollution accounts for an estimated several billion dollar crop loss every year in the United States alone, and research and analysis suggests that about 90% of this crop loss can be directly or indirectly attributed to ozone (Tingey *et al.*, 1994). Evidence also indicates that ozone may cause short- and long-term damage to the growth of forest trees, (McLaughlin and Downing, 1995) as well as altering the biogenic hydrocarbon emissions of vegetation (Mehlhorn, 1989).

4.2.3.2 Tropospheric Photochemistry and Ozone Formation

In the lowest part of the atmosphere, chemical interactions are very complex. A large number of chemical compounds are present, the levels of many of these compounds are greatly elevated, and emissions vary rapidly due to both natural and anthropogenic sources. Ozone formation in the troposphere results from non-linear interactions between NO_X, VOCs, and sunlight (NRC, 1991; Seinfeld and Pandis, 1998). In remote regions, ozone formation is driven essentially by methane, (14) however elsewhere most VOCs participate in ozone generation. For example, measurements of non-methane organic compounds in the South Coast Air Basin of California during the 1987 Southern California Air Quality Study identified more than 280 ambient hydrocarbon and oxygenated organic species, (Lurmann and Main, 1992) many of which originated from solvents and contribute in differing degrees to ozone generation.

The only significant process forming O_3 in the lower atmosphere is the photolysis of NO_2 (reaction with sunlight), followed by the rapid reactions of the oxygen atoms formed with O_2.

$$NO_2 + hv \rightarrow O(^3P) + NO \qquad (4.7)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

This is reversed by the rapid reaction of O_3 with NO,

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (4.8)$$

This reaction cycle results in a photostationary state for O_3, where concentrations only depend on the amount of sunlight available, dictated by the NO_2 photolysis rate (k_1) and the $[NO_2]/[NO]$ concentration ratio.

$$[O_3]_{steady-state} = \frac{k_1[NO_2]}{k_2[NO]} \quad (4.9)$$

Because of this photostationary state, ozone levels generally rise and fall with the sun, behavior that is referred to as "diurnal."

If the above NO_x cycle were the only chemical process at work, the steady-state concentrations of ozone would be relatively low. However, when VOCs such as organic solvent compounds are present, they react to form radicals that may either (1) consume NO or (2) convert NO to NO_2. This additional reaction cycle combined with the above photostationary state relationship causes O_3 to increase.

Although many types of reactions are involved (Atkinson, 1990; NRC, 1991; Atkinson, 1994; Seinfeld and Pandis, 1998), the major processes for most VOCs can be summarized as follows:

$VOC + OH \rightarrow RO_2 + products$ (4.10a)

$RO_2 + NO \rightarrow NO_2 + radicals$ (4.10b)

$radicals \rightarrow ... \rightarrow OH + products$ (4.10c)

$products \rightarrow ... \rightarrow ... + CO_2$ (4.10d)

The last two pseudo-reactions given comprise many steps, and the products often include formaldehyde, carbon monoxide and organonitrates. The rate of ozone increase caused by these processes depends on the amount of VOCs present, the type of VOCs present, and the level of OH radicals and other species with which the VOCs can react. One of the major determinants of a compound's impact on ozone is the rate of the reaction of the particular VOC with the hydroxyl radical via reaction 4.2.10a, above. The

total amount of ozone formed is largely determined by the amount of VOC and NO, available.

The dependence of O_3 production on the initial amounts of VOC and NO_x is frequently represented by means of an ozone isopleth diagram. An example of such a diagram is shown in Figure 4.1. The diagram is a contour plot of ozone maxima obtained from a large number of air quality model simulations using an atmospheric chemical mechanism. Initial concentrations of VOC and NO_x are varied; all other variables are held constant. Notice that there is a "ridge" along a certain VOC-to-NO, ratio where the highest ozone concentrations occur at given VOC levels. This is referred to as the "optimum" VOC-to- NO_x ratio. While the atmosphere is more complicated than this idealized system, important features are very similar.

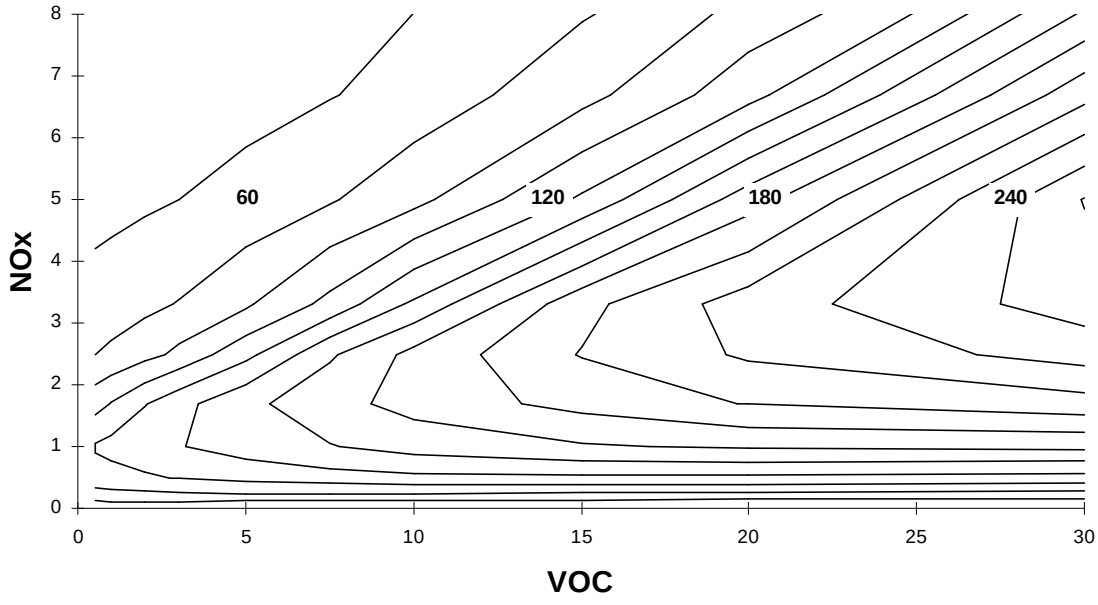


Figure 4.1. Ozone isopleth diagram of constant concentration showing the dependencies of ozone on varying levels of initial VOCs and NO_x. Concentrations are given in ppb. [Adapted from Bergin et al., *Encyclopedia of Environmental Analysis and Remediation*, 3355, (1998)]

VOC-to- NO_x ratios sufficiently low to retard ozone formation from an optimum ratio (represented in the upper left quadrant of Figure 4.1) can occur in central cities and in plumes immediately downwind of strong NO_x sources. Rural environments tend to be characterized by fairly high VOC-to- NO_x ratios because of the relatively rapid removal of NO from non-local sources as compared to that of VOCs, coupled with the usual absence of strong local NO_x sources and the presence of natural VOC sources. In such rural environments, the formation of ozone is limited more by the absence emissions of NO_x, and most ozone present was directly transported from upwind. Indeed, in most of the troposphere, except in areas of strong NO_x sources, the availability of NO_x governs ozone production.

4.2.3.3 Assessing solvent impacts on ozone and VOC reactivity

As mentioned previously, the contribution of solvents to the VOC levels, and hence ozone formation, is significant. For example, in Los Angeles, about 25% of the VOC mass is from solvent use (SCAQMD, 1997). This fraction is down from earlier years due to various controls such as using water-based paints and enclosing/controlling paint spraying operations. On the other hand, reduction in the use of CFCs as propellants has led to an increase in organic emissions from substituted compounds (Derwent and Pearson, 1997). However, the impact on ozone formation by a specific source is not directly proportional to the amount of VOC emitted by that source. A major determinant of the ozone forming potential is the reactivity of the compound or compound mixture emitted. Reactivity can be viewed as the propensity for a compound to form ozone, and this propensity varies dramatically between compounds and between environments (Carter, 1990a; Carter, 1991).

As seen in Table 4.1, ‘box’ model (single cell) simulations designed to represent summertime conditions in Los Angeles, California indicate that the amount of carbon associated with each class of compound only roughly corresponds to the amount of ozone

formed from those compounds. Methane, which reacts very slowly but comprises most of the carbon, contributes little to ozone formation. Alkenes and aromatics are only a small part of the total carbon, but lead to much of the ozone formation.

Table 4.1. Percentage of ozone production attributable to each organic. The percentages shown should be viewed as only approximate, and will depend upon local emissions characteristics. [Adapted from F.M. Bowman and J.H. Seinfeld, J Geophys. Res., 99, 5309, (1994), and M.S. Bergin et al., *Env. Sci. Technol.*, 29, 3029 (1998)]

Compound Class	**Percent of carbon in each specified class**	**Percent of ozone due to specified organic class**
carbon monoxide*	35	6
methane	40	1
aldehydes and ketones	1	3
non-methane alkanes, -4C	8	17
non-methane alkanes, -8C	5	16
aromatics, including toluene	3	5
aromatics, including xylenes and others	3	13
ethene	2	12
biogenic alkenes and isoprene	1	10
other alkenes	2	17

* While not considered organic carbon, carbon monoxide acts to facilitate ozone formation similar to organic compounds.

4.2.3.3.1. Quantification of the Effect of Solvent Emissions on Ozone Formation

Two methods are generally employed to quantify the role pollutants play in forming ozone: experimental and computational. Both types of estimation approaches have their limitations. In the case of physical experiments, it is difficult to fully simulate ambient conditions, so the results do not have general applicability. In the case of computational approaches, uncertainties and approximations in the model for airshed conditions, in its formulation, and in the chemical mechanism cause uncertainties in the predicted ozone impacts. For these reasons, modeling predictions and experimental measurements are used together.

4.2.3.3.2 Experimental Analysis

Experimental analysis is performed using environmental 'smog' chambers, either with a series of single hydrocarbons irradiated in the presence of NO_x or using complex mixtures to simulate, for example, automobile exhaust emitted into characteristic urban ambient conditions. Such chambers are large reaction vessels (some with internal volumes of cubic meters), in which air and small amounts of hydrocarbons and NO_x are injected, and then irradiated with real or artificial light. Both indoor and outdoor chambers are used so behaviors can be evaluated under natural radiative conditions and under controlled conditions. While these experiments (Carter and Atkinson, 1989; Carter, 1990a; Carter, 1991; Carter, 1995; Kelly and Wang, 1996; Bergin *et al.*, 1998a) clearly indicate differences in ozone formation from individual hydrocarbons, they do not represent some important physical systems of urban pollution such as the mixing processes and continuing emissions cycles. Such experiments have focused both on groups of compounds as well as specific VOCs, including solvents. A particular limitation has been studying very low vapor pressure solvents because it is difficult to get enough of the compound into the vapor phase in the chamber to appreciably change the ozone levels. Another limitation is the expense of using smog chambers to simulate a

large range of conditions that might occur in the atmosphere. On the other hand, smog chambers are very powerful, if not fundamental, for developing chemical mechanisms that describe the reaction pathways that can be used in computational approaches.

4.2.3.3.3 Computational Analysis (Air Quality Models)

Given the limitations of physical experiments to simulate atmospheric conditions, computer models have been developed to assess the impact of emissions on ozone. These models, called airshed models, are computerized representations of the atmospheric processes responsible for air pollution, and are core to air quality management (Bergin *et al.*, 1998a). They have been applied in two fashions to assess how solvents affect ozone. One approach is to conduct a number of simulations with varying levels of solvent emissions (Derwent and Pearson, 1997). The second approach is to evaluate individual compounds and then calculate the incremental reactivity of solvent mixtures (Carter, 1991; Derwent and Jenkin, 1991; Bowman and Seinfeld, 1994; Carter, 1994; Bergin *et al.*, 1995; Carter, 1995; Khan *et al.*, 1999).

Derwent and Pearson (1997) examined the impact of solvent emissions on ozone by simulating air parcel trajectories ending in the United Kingdom and perturbing the emissions to account for an anticipated 30% mass reduction in VOCs from solvents between 1995 and 2007. They found a small decrease in ozone-from 78 to 77 ppb in the mean peak ozone in the UK, and a 9 ppb reduction from 129 ppb outside of London. A more substantial decrease of 33 ppb from the 129 ppb peak outside of London was found from reducing non-solvent mass VOC emissions by 30% outside of the UK and 40% within the UK. This suggests that the VOC emissions from sources other than solvents have a higher average reactivity, as is discussed by McBride et al. (McBride *et al.*, 1997).

While the types of simulations conducted by Derwent and Pearson (1997) are important to understanding the net effect of solvent emissions on ozone, there is an unanswered associated and important question, that being which specific solvents have

the greatest impacts. This question is critical to assessing if one solvent leads to significantly more ozone formation than a viable substitute (or vice versa).

To evaluate the contribution of individual organic compounds to ozone formation, the use of incremental reactivities (IR) was proposed, (Carter and Atkinson, 1989; Carter, 1990a; Carter, 1991; Carter, 1995) defined as the change in ozone caused by a change in the emissions of a VOC in an air pollution episode. To remove the dependence on the amount of VOC added, incremental reactivity is defined by equation 4.11 as the limit as the amount of VOC added approaches zero, i.e., as the derivative of ozone with respect to VOC:

$$IR_i = \frac{\partial[O_3]}{\partial[VOC_i]} \tag{4.11}$$

Here, IR_i is the incremental reactivity, and the subscript i denotes the VOC being examined. This definition takes into account the effects of all aspects of the organic's reaction mechanism as well as the effects of the environment where the VOC is emitted. A similar quantity is relative reactivity (Bergin *et al.*, 1998a) RR_i:

$$RR_i = \frac{IR_i}{\sum_{j=1}^{N} F_{Bj} IR_j} \tag{4.12}$$

where: F_{Bj} mass fraction of compound j in a reference mixture, and

IR incremental reactivity of species i or j (grams ozone formed per gram compound i or j emitted)

In this case, the incremental reactivity is normalized by the reactivities of a suite of organics, thus removing much of the environmental dependencies found when using IRs defined by equation 4.11. This metric provides a means for directly comparing individual compounds to each other in terms of their likely impact on ozone.

A number of investigators have performed calculations to quantify incremental and/or relative reactivities for various solvents and other organics [(Derwent and Jenkin, 1991; Bowman and Seinfeld, 1994; Carter, 1994; Bergin *et al.*, 1998a; Bergin *et al.*, 1998b; Khan *et al.*, 1999; Carter, 2006) and references therein]. Those studies found very similar results for the relative reactivities of most compounds found in solvents. Figure 4.2 [based on references (Bergin *et al.*, 1995; Bergin *et al.*, 1998a; Khan *et al.*, 1999)] shows the relative reactivities for some of the more common compounds, as well as possible solvent substitutes and isoprene, a naturally emitted organic. [For a more extensive list of relative reactivities, see (Carter, 1991; Carter, 1994; Carter, 2006).] As can be seen, even normalized compound reactivities can vary by orders of magnitude. Some compounds even exhibit "negative" reactivities, that is that their emission can lead to ozone decreases under specific conditions. In particular, negative reactivities are found most commonly when the levels of NO_x are low, e.g., in non-urban locations. For example, Kahn et al. (1999) found that a solvent can promote ozone formation in one area (e.g., near downtown Los Angeles), but retard ozone formation further downwind. Kahn also found that the relative reactivities of the eight different solvents studied were similar in very different locations, e.g., Los Angeles, Switzerland and Mexico City.

Looking at Figure 4.2, it is apparent that alkenes and aromatic hydrocarbons with multiple alkyl substitutions (e.g., xylenes and tri-methyl benzene) have relatively high reactivities. Alcohols, ethers and alkanes have lower reactivities. Halogenated organics have some of the lowest reactivities, so low that they are often considered unreactive. This suggests that there are two ways to mitigate how solvents contribute to air quality problems. The more traditional method is to reduce the mass of organic solvent

emissions (e.g., by using water-based paints). A second approach is to reduce the overall reactivity of the solvent used, e.g., by switching to ethers, alcohols, alkanes or halogenated compounds. Solvent substitution, however, is complicated by the need to maintain product quality.

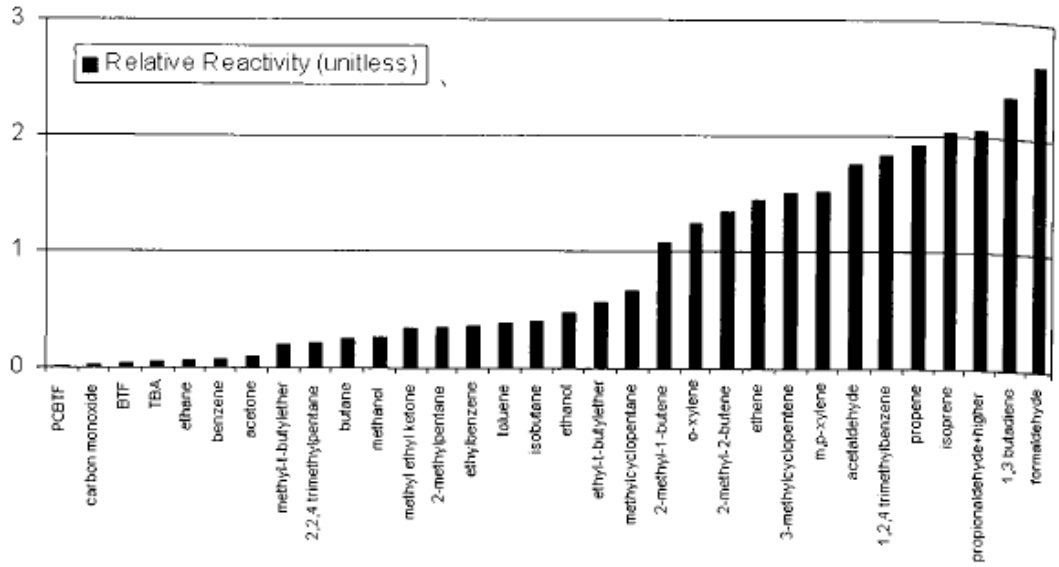


Figure 4.2. Solvent relative reactivities based on mass of ozone formed per gram of solvent emitted into the gas phase. PCBTF is para-chlorobenzo-trifluoride, BTF is benzo-trifuoride and TBA is tertiary butyl acetate. [Adapted from M.S. Bergin et al., *Env. Sci. Technol.*, 29, 3029 (1998) and M. Khan et al., *Atmos. Env.*, 33, 1085 (1999)].

4.2.4 Regulatory Approaches to Ozone Control and Solvents

Historically, regulatory approaches to reducing ozone concentrations have relied on reducing the mass emissions of VOCs (NRC, 1991; Derwent and Pearson, 1997), and this has led to stringent controls on solvents. Two factors are important in determining if an organic solvent is considered a VOC: its reactivity (discussed above) and its vapor pressure. In the U.S., traditionally, if a compound was less reactive than ethane, it was considered unreactive. Such compounds include many halogenated species and some

acetates and ethers. Recently, acetone was also added as an unreactive compound. A vapor pressure threshold is also used in many areas (e.g., Europe) since it is viewed that compounds with very low vapor pressures will not be emitted rapidly into the atmosphere. It has been argued that a vapor pressure limit may not be appropriate since, given time, even lower vapor pressure compounds will have ample time to evaporate. Recently, California began considering regulations that more fully account for the full range of reactivities that solvents possess. This is due, in part, to an effort make it easier for manufacturers to meet stringent regulations being adopted in that state for meeting air quality goals. It is likely that other areas will also have to employ increasingly more stringent regulations, to both lower ozone and alleviate other environmental damage.

In many countries, greater focus is now being placed on reducing NO_x emissions to mitigate ozone formation. This has important ramifications for solvent use, indicating that regulatory focus is now turning from VOCs towards NO_x, the other main precursor to ozone. Another imminent regulatory issue is the control of ambient fine particulate matter. While the role of solvent emissions in forming particulate matter is not well understood, studies to date do not suggest they are a major contributor.

4.2.5 Summary

Solvents are, and will continue to be, one of the major classes of organic compounds emitted into the atmosphere. These compounds have a wide range of air quality impacts. Accumulation of toxic compounds indoors is of concern, although outdoors the concern of toxicity is significantly less substantial due to rapid dilution. In the stratosphere, some of the halogenated solvents lead to depletion of the protective layer of ozone, while in the troposphere, solvents generally lead to increased ozone levels, where it adversely affects health and the environment. The former has led to regulations of CFCs, and the latter to regulations of organic solvents. Some solvents are also considered to be precursors to the formation of secondary tropospheric pollutants

other than ozone, such as particulate matter, however these relationships are currently less certain.

In the aggregate, total emissions from solvents in the U.S. are the second largest single-source VOC category in polluted urban areas, falling just behind motor vehicle VOC emissions both in terms of mass and of urban ozone production. For now, regulations are designed to reduce the loss of ozone in the stratosphere and the formation of excess ozone in the troposphere. However, while some solvents are very reactive, others are substantially less reactive, suggesting that there is considerable opportunity to reduce urban ozone formation from solvents by utilizing substitutes with low ozone forming potentials. Currently, most regulations are targeted at reducing the mass of VOC emissions, not their relative impacts on ozone.

REFERENCES

Atkinson, R. (1990). *Atmos. Environ.* **24A**: 1.

Atkinson, R. (1994). *J Phys. Chem.*(Ref Data, Monograph No. 2).

Bergin, M.S. and Russell, A.G. (2001). Organic Solvent Impacts on Tropospheric Air Pollution. In Handbook of Solvents. G. Wypych. New York, ChemTec**:** 1188-1200.

Bergin, M.S., Russell, A.G., Carter, W.P.L., Croes, B. and Seinfeld, J.H. (1998a). VOC Reactivity and Urban Ozone Control. In Encyclopedia of Environmental Analysis and Remediation. J. W. Sons. New York**:** 3355-3383.

Bergin, M.S., Russell, A.G. and Milford, J.B. (1995). "Quantification of Individual Voc Reactivity Using a Chemically Detailed, 3-Dimensional Photochemical Model." *Environmental Science & Technology* **29**(12): 3029-3037.

Bergin, M.S., Russell, A.G. and Milford, J.B. (1998b). "Effects of chemical mechanism uncertainties on the reactivity quantification of volatile organic compounds using a three-dimensional air quality model." *Environmental Science & Technology* **32**(5): 694-703.

Bowman, F.M. and Seinfeld, J.H. (1994). *J. Geophysical Research* **99**: 5309.

Carter, W.P.L. (1990). *Atmos. Environ.* **24**(A): 481.

Carter, W.P.L. (1991). Development of Ozone Reactivity Scales for Volatile Organic Compounds, EPA 600/3-91-050. U.S. Environmental Protection Agency. Research Triangle Park, NC

Carter, W.P.L. (1994). "Development of Ozone Reactivity Scales for Volatile Organic Compounds." *Journal of the Air and Waste Management Assoc.* **44**: 881-899.

Carter, W.P.L. (1995). "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic-Compounds." *Atmospheric Environment* **29**(18): 2513-2527.

Carter, W.P.L. (2006). Downloadable Documents. CE-CERT, Univ. of CA, Riverside. http://pah.cert.ucr.edu/~carter/bycarter.htm (Accessed: Oct., 2006).

Carter, W.P.L. and Atkinson, R. (1989). "Computer Modeling Study of Incremental Hydrocarbon Reactivity." *Environmental Science & Technology* **23**(7): 864-880.

Chameides, W.L., Kasibhatla, P.S., Yienger, J. and Levy, H. (1994). "Growth of Continental-Scale Metro-Agro-Plexes, Regional Ozone Pollution, and World Food-Production." *Science* **264**(5155): 74-77.

Derwent, R.G. and Jenkin, M.E. (1991). *Atmos. Environ.* **25**(A): 1661-1673.

Derwent, R.G. and Pearson, J.K. (1997). *Environ. Technol.* **18**: 1029.

E-PRTR (2006). The European Pollutant Release and Transfer Register. Munich, Germany. "Diffuse Sources". http://www.bipro.de/__prtr/sub/database_air.htm (Accessed: Oct., 2006).

EPA (2005). U.S. Environmental Protection Agency, Technology Transfer Network. Clearinghouse for Inventories and Emissions Factors (ChIEF). "National Emissions Inventory (NEI) Air Pollutant Emissions Trends Data. Data file VOC07182005." http://www.epa.gov/ttn/chief/trends/index.html (Accessed: Oct., 2006).

Horvath, S.M. and McKee, D.J. (1994). Chapter 3. Acute and chronic health effects of ozone. In Tropospheric Ozone: Human Health and Agricultural Impacts. D. J. McKee. Boca Raton, FL, CRC Press/Lewis Publishers**:** 39-83.

IPCC (1996). Climate Change 1995: The Science of Climate Change. Contribution of Working Group I to the Second Assessment Report. Cambridge University Press. Intergovernmental Panel on Climate Change. Cambridge, Great Britain.

Kelly, N.A. and Wang, P. (1996). Part I: Indoor Smog Chamber Study of Reactivity in Kelly, N.A.; Wang, P.; Japar, S.M.; Hurley, M.D.; and Wallington, T.J. (1996). Measurement of the Atmosphere Reactivity of Emissions from Gasoline and

Alterative-Fueled Vehicles: Assessment of Available Methodologies, Second-Year Final Report. Environmental Research Consortium. Coordinating Research Council Contract No. AQ-6-1-92 and National Renewable Energy Laboratory Contract No. AF-2-112961.

Khan, M., Yang, Y.J. and Russell, A.G. (1999). "Photochemical reactivities of common solvents: comparison between urban and regional domains." *Atmospheric Environment* **33**(7): 1085-1092.

Lippmann, M. (1991). "Health-Effects of Tropospheric Ozone." *Environmental Science & Technology* **25**(12): 1954-1962.

Lippmann, M. (1993). *J. Exp. Anal. Environ. Epidemiol.* **3**(1): 103-129.

Lurmann, F.W. and Main, H.H. (1992). Analysis of the Ambient VOC Data Collected in the Southern California Air Quality Study. Final Report, Contract A832-130. California Air Resources Board. Sacramento, CA.

McBride, S.J., Oravetz, M.A. and Russell, A.G. (1997). "Cost-benefit and uncertainty issues in using organic reactivity to regulate urban ozone." *Environmental Science & Technology* **31**(5): A238-A244.

McLaughlin, S.B. and Downing, D.J. (1995). "Interactive Effects of Ambient Ozone and Climate Measured on Growth of Mature Forest Trees." *Nature* **374**(6519): 252-254.

Mehlhorn, W. (1989). *Nature* **327**: 417.

NRC (1991). Rethinking the Ozone Problem in Urban and Regional Air Pollution. Washington, D.C., National Research Council, National Academy Press.

OTA (1989). Catching Our Breath: Next Steps for Reducing Urban Ozone, OTA-O-412, U.S Government Printing Office. U.S. Congress, Office of Technology Assessment. Washington, DC.

SCAQMD (1997). Air Quality Management Plan. South Coast Air Quality Management District. http://www.aqmd.gov/aqmp/97aqmp/index.html

Seinfeld, J.H. and Pandis, S.N. (1998). Atmospheric Chemistry and Physics. New York, John Wiley & Sons, Inc.

Tingey, D.T., Olszyk, D.M., Herstrom, A.A. and Lee, E.H. (1994). Chapter 6. Effects of Ozone on Crops. In Tropospheric Ozone: Human Health and Agricultural Impacts. D. J. McKee. Boca Raton, FL, CRC Press/Lewis Publishers**:** 175–206.

4.3 The Development and Expansion of Regulatory Applications Accounting for the Ozone Formation Potentials of Volatile Organic Compounds

This section includes the following two publications, provided as Appendices B and C respectively:

> Bergin, M., W. P. L. Carter, J. Milford, P. J. Ostrowski and A. G. Russell (1999). Reactivity Assessments. Final Report to the Relative Reactivity Working Group. Available from: http://www.narsto.org/section.src?SID=10

> Hakami, A., M.S. Bergin, and A.G. Russell, **2004**. "Ozone formation potential of organic compounds in the eastern United States: A comparison of episodes, inventories, and domains", *Environmental Science & Technology*, **33**(24), 6748-6759.

4.3.1 History of Ozone Management

One of the important setbacks experienced in our efforts to control urban pollution resulted from an incomplete understanding of the ambient concentrations, sources, and chemistry of organic compounds and their relation to ozone formation. Significant health impacts from elevated ozone concentrations were recognized early on; however the secondary, photochemical nature of ozone formation and its dependence on ambient conditions made identification of source contributions difficult. While scientists recognized that individual VOC contributions to ozone formation vary, these contributions were not easily characterized. Initial ozone control efforts focused on reducing the total mass of anthropogenic VOC emissions regardless of differences in their ozone formation potential, or 'reactivity', and few control efforts targeted NO_x emissions, the companion precursor to tropospheric ozone formation.

Disappointing progress in ozone pollution reduction, coupled with research findings that anthropogenic hydrocarbon emissions were significantly underpredicted (NRC, 1991) and that hydrocarbons emitted by natural sources contributed significantly to ozone production in some cities (Chameides *et al.*, 1988) initiated the development of control strategies in the early 1990s aimed at reductions in NO_x emissions, resulting in some significant progress in ozone abatement. However, ozone is often most immediately responsive to VOC reduction until NO_x levels are significantly lowered (e.g. Figure 1.2), and ozone concentrations in many areas continued to exceed the NAAQS. In particular, many highly populated areas with the worst ozone problems were found to require both VOC and NO_x emission reductions to reduce ozone to within the NAAQS.

4.3.2 Barriers to Accounting for Reactivity in Regulatory Application

The amount of ozone formed from a given quantity of a VOC is heavily dependent on the local ambient conditions, including the meteorology (wind speed, temperature, mixing height and humidity), pollutant transport (the residence time of emissions in an urban area), distribution of emissions sources (e.g., proportion of biogenic, mobile source, and other emissions), and background pollutant concentrations (e.g., the VOC/NO_x ratio and the absolute levels of VOCs and NO_x). As our understanding of the chemistry of ozone formation and of the physical and chemical composition of airsheds around the country improved, scientists were able to begin classifying which VOCs contributed more significantly to ozone production. Some of the initial barriers to accounting for reactivity in regulations were (a) deciding how to quantify reactivity, (b) determining if uncertainties associated with the quantification measures outweighed the differences in reactivity for most of the common or highly reactive emitted compounds, and (c) evaluating how reactivity varied with location. The quantification of reactivity was introduced in the previous section of this chapter, and all

three topics are discussed in detail in Appendix B (Bergin *et al.*, 1999a) and are briefly summarized here.

4.3.2.1 Quantification of Reactivity

A number of methods have been utilized to quantify the impact of a VOC on ozone formation, including laboratory experiments, comparison of the OH initiation rate constants, and computational modeling. While results from all methods have aided in understanding and evaluation, general consensus has accepted model derived reactivity quantification measures as the most representative of what occurs in the atmosphere (Tonnesen *et al.*, 1998). In particular, normalized maximum incremental reactivity (MIR) values (as described previously and in Appendix B) are currently accepted as the most applicable, reliable, and relevant measures for regulatory application. The MIR of a compound is defined at the highest IR value for that compound (described in part 1 of this chapter), which occurs under relatively high NO_x conditions, representative of polluted areas where VOC control is most effective . The MIR scale by William P.L. Carter (Carter, 1994) and its updates have been the only reactivity scale utilized in regulations to date.

The Carter MIR values were originally calculated using a Lagrangian trajectory model, incorporating trajectories with conditions representative of 39 major cities. Although these types of models oversimplify transport and diffusion, and provide limited information on spatial variability, they can represent explicit chemical detail and have low input data and computational requirements. These properties made Lagrangian models the best choice for early calculations of reactivity and uncertainty analysis. Subsequently, increased computational capabilities allowed the utilization of more explicit chemical mechanisms in Eulerian models for analysis of reactivity at the urban scale (Bergin *et al.*, 1998a), however the use of Brute-Force (B-F; described in Chapter 3) still computationally limited these applications.

Recent enhancements in sensitivity techniques (DDM-3D) and increased geographic scale in the URM-1ATM model (described previously) has now facilitated evaluation of reactivity at the regional scale [(Hakami *et al.*, 2004a), in Appendix C]. In addition to allowing for the reactivity quantification of a large number of explicit species on a scale incorporating wide range of ambient conditions, the use of DDM provides a measure of reactivity for very small changes in concentration. When small perturbations are evaluated using B-F, predictions may be unreliable due to levels of uncertainty higher than the predicted response or from the effects of 'numerical noise' resulting from the application of numerical techniques. Because some compounds may have a very high reactivity but are emitted in low concentrations, the evaluation of very small changes (i.e. the derivative calculated using DDM) provided by this study are useful for comparison with other reactivity measures.

Results from the regional scale application (e.g. Figure 4.3) provide measures for 32 explicit and 9 lumped compounds, calculating the reactivities relative to a mixture representative of total anthropogenic VOC emissions in the United States. Relative reactivity measures from this study are fairly robust and consistent between the episodes, and result in rankings similar to the Carter MIR scale, but with a more narrow range for some of the higher reactive species such as aldehydes. The VOC compounds evaluated in most reactivity quantification studies include organics found in motor vehicle exhaust and in common organic solvents, typically the two largest sources of anthropogenic VOC emissions in polluted areas.

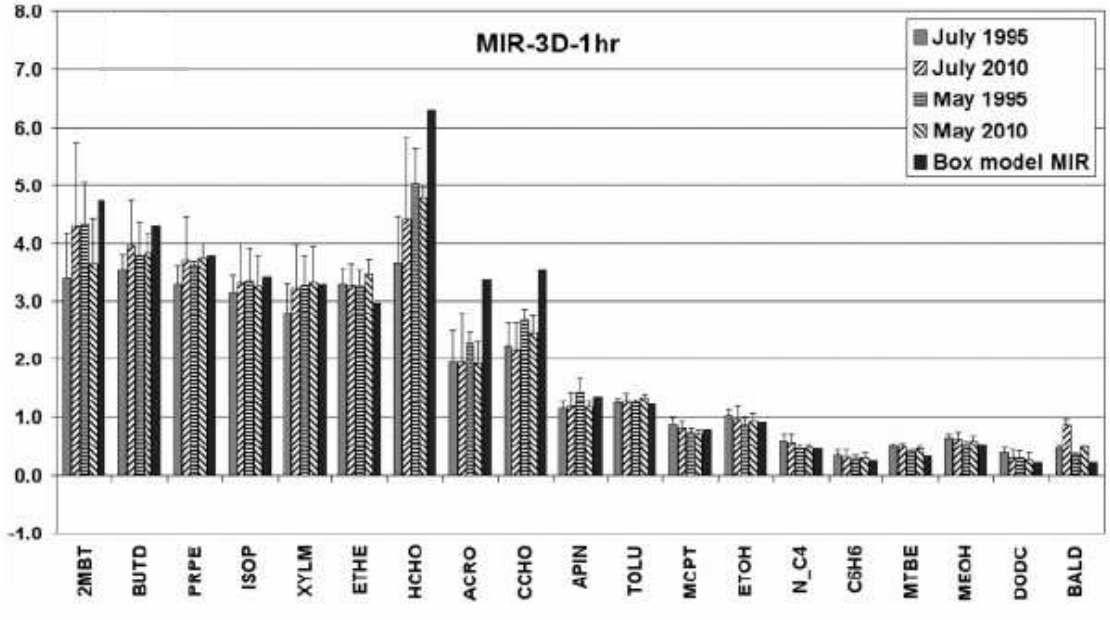


Figure 4.3. Comparison of MIR 1-hour average ozone reactivity metrics for each episode calculated using the URM-1ATM with DDM-3D, and comparison with the corresponding Carter MIR values.

4.3.2.2 Uncertainty

While computational models are the best tools currently available for quantifying reactivity, uncertainties in model components and input data impact model predictions of reactivity (Tonnesen *et al.*, 1998; Bergin *et al.*, 1999a). In particular, the chemical mechanisms and emissions inventories used in the models have significant uncertainties, which cause corresponding uncertainty in the reactivity estimates. At issue is the extent to which the uncertainties impact the reactivity calculations. Integrated studies applying single-cell, Lagrangian, and Eulerian computational models utilizing different chemical mechanisms have compared quantification measures (McNair *et al.*, 1992; Milford *et al.*, 1992; Russell *et al.*, 1995; Yang *et al.*, 1995; Bergin *et al.*, 1996; Bergin *et al.*, 1998a; Bergin *et al.*, 1998b; Martien *et al.*, 2003) and have evaluated the effect of important uncertainties on the predictions (Russell *et al.*, 1995; Bergin *et al.*, 1998a; Bergin *et al.*,

1999a; Derwent, 2004). Overall, specific relative reactivity scales are found to be stable in the relative ranking of the individual compounds. Using results from different model and chemical mechanism formulations benefits from the strengths of each modeling approach while increasing confidence in the robustness of the predictions (Bergin *et al.*, 1999a).

Modeling studies have previously utilized either B-F or DDM to evaluate uncertainty. A novel approach to uncertainty evaluation of ozone predictions and comparison of the efficiency and associated uncertainty of NO_x versus VOC control on ozone reduction is the application of a Bayesian Monte Carlo analysis with a Langrangian air quality model (Bergin *et al.*, 1999b; Bergin and Milford, 2000). Use of this technique for evaluation of uncertainty effects on reactivity measures would be beneficial. Overall, significant progress has been made on uncertainty analysis, however some serious concerns remain and simulation results must always be evaluated with the knowledge that the predictions are our best estimates and not a direct representation of atmospheric behavior (Oreskes *et al.*, 1994; Russell and Dennis, 2000; Fine *et al.*, 2003).

4.3.2.3 Variability

Another important barrier to accounting for reactivity in ozone control regulations is that the absolute amount of ozone formed from a given quantity of VOC is heavily dependent on the local ambient conditions, in particular the VOC to NO_x ratio (Bergin *et al.*, 1999a). For example, in the extreme, a compound can go from being fairly reactive under certain conditions to having a negative reactivity under others (e.g. toluene). This variability may limit the use of generalized reactivity weighting and the development of reactivity-based control strategies. However, studies to date indicate that most organics that are highly reactive under one set of conditions (relative to the other VOCs) remain highly reactive under other conditions. Likewise, the less reactive VOCs remain relatively less reactive. Compounds that vary widely are found to be the

exception rather than the rule. As discussed above, this variation is reduced by the use of normalizing and relative ranking in the reactivity quantification of VOCs (Carter, 1994a; Bergin et al., 1995, 1997; Russell et al., 1995), though species reactivities do vary in regions of low NO_x availability or very high VOC levels. Comparison between reactivity studies using different modeling domains increases our confidence in the applicability of reactivity scales for different geographic regions (Bergin *et al.*, 1999a; Khan *et al.*, 1999; Hakami *et al.*, 2004a). The recent regional-scale modeling applications have provided reactivity measures over large contiguous domains, incorporating a wider variety of environmental conditions than previous simulations.

4.3.3 Regulatory Applications and Future Potential Applications

4.3.3.1 Alternative Fuel Reactivity Adjustment Factors

The first regulations accounting for reactivity were adopted by the California Air Resources Board (CARB) in 1990 as part of a plan to 'level the playing field' for entry to the market by alternatively fueled vehicles(CARB, Apr 1992; CARB, Aug 1990). Rather than comparing the total mass of exhaust VOCs from each fuel, CARB wanted to account for the impact the characteristic mixture of VOCs from each fuel would have on ozone formation. Each alternative fuel was assigned a Reactivity Adjustment Factor (RAF), defined as the ratio of the reactivity of the alternative fuel to the reactivity of a base fuel. The reactivity of each fuel f was calculated as:

$$reactivity_f = \sum_{i=1}^{N} mass_i R_i \qquad (4.13)$$

where, for each organic species *i* in the fuel exhaust (1 to N), the mass is multiplied by the reactivity of the species. The RAF was then used to determine the allowable mass of VOC in alternatively fueled vehicle exhaust. Ultimately, the Carter MIR values were chosen to quantify R for the designation of the fuel RAFs. The effects of uncertainties in

RAFs due to rate constants and product yields was not found to alter the ranking of the fuels evaluated (Bergin *et al.*, 1996). The impact of environmental variability on RAFs was also investigated for six fuels across 39 urban trajectories. The variation in absolute ozone forming potentials across cities was substantial; however when reactivities were normalized (e.g. the RAF), variation was sharply diminished (Russell *et al.*, 1995). This marked decrease in variability may not be possible through normalizing for source types emitting fewer compounds than that in vehicle exhaust.

4.3.3.2 Aerosol Coatings

In 2000, in cooperation with industry, CARB proposed an amendment to extend the reactivity-weighting approach from alternatively-fueled vehicle exhaust to regulations controlling aerosol coating products, stating "[w]e believe this control approach has the potential to provide more flexibility to manufacturers, at less cost than traditional mass-based VOC controls, while achieving equivalent or greater air quality benefits."(CARB, 2000) In addition to using the MIR scale to account for differences in reactivity, the amendment accounts for the estimated degree of uncertainty associated with each value. A positive multiplying factor based on the estimated uncertainty is applied to each value, and can be decreased as new or improved data becomes available. In California, over 80 percent of VOCs by mass currently used in aerosol coatings have MIR values with low enough associated uncertainty that no multiplying factor is required. (CARB, 2000; CARB, 2004)

In September 2005, the EPA published a Final Rule that approved the reactivity adjusted emissions reductions in the California SIP, paving the way for similar regulations in the future (EPA, 2005c; PCA Services, 2006). The EPA and interested industry groups are currently discussing the possibility of a National Aerosol Coatings Rule that would be very similar to the CARB reactivity-based rule (PCA Services, 2006).

4.3.3.3 Industrial Stack Emissions

In December 2000, the Texas Commission on Environmental Quality (TCEQ) adopted an ozone SIP for the 'Severe' ranked nonattainment area of Houston-Galveston-Brazoria (HGB), requiring a 90% average reduction in NO_x from industrial sources. The Business Coalition for Clean Air - Appeal Group (BCCA-AG) challenged the SIP, contending, among other things, that the last 10% of the NO_x reductions were not cost effective and that the ozone plan would fail (TCEQ, 2006b). As part of the settlement, the TCEQ conducted an evaluation of ground-level ozone in the HGB and east Texas areas and identified four organic compounds as frequently responsible for high reactivity days and 1-hour ozone exceedances. These four compounds, ethylene, propylene, 1,3-butadiene, and butenes, termed highly reactive VOCs (HRVOCs), are largely emitted from four key industrial sources: fugitives, flares, process vents, and cooling towers. Photochemical grid modeling results indicate that limiting emissions of HRVOCs in conjunction with an 80% reduction in NO_x has an equivalent or better 1-hour air quality benefit than that resulting from a 90% reduction in point source NO_x alone.

In December 2004, the TCEQ established the Highly-reactive volatile organic compound Emissions Cap and Trade (HECT) program, providing flexibility in regulatory compliance for facilities located in HGB nonattainment area that emit more than ten tons per year of HRVOCs from process vents and cooling-tower heat exchangers. The HECT program, which begins on January 1, 2007, establishes a mandatory annual HRVOC emissions cap, and sites subject to the program are required to possess an allowance for each ton of HRVOC emitted. Sites have the option of trading excess HRVOC allowances on the open market within a specific trading zone. An issue of concern arises from ambient monitoring results showing that other less-reactive VOCs sometimes contribute an equivalent amount of reactivity to the airshed as the HRVOCs. The reactivity measure applied does not incorporate the speed at which a VOC contributes to ozone formation, and while HRVOCs react quickly, thus making them the most

important VOCs with regard to the 1-hour ozone standard, other VOCs can lead to more ozone over time. Additional VOC controls may be necessary to achieve the 8-hour ozone standard (TCEQ, 2006a).

4.3.3.4 Extension of Reactivity Weighting Applications

4.3.3.4.1 EPA Support for Reactivity Accounting in SIPs

In 2003, the U.S. EPA released an Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans (EPA, 2003a). In this memorandum, the EPA encourages States, particularly those with persistent ozone nonattainment problems, to consider incorporating VOC reactivity into the development of their ozone control strategies. The EPA notes that the use of reactivity information may be able to improve the effectiveness and efficiency of VOC control policies. In addition, the EPA encourages parties to work through the Reactivity Research Working Group (RRWG), described below, to improve the scientific foundation for reactivity-based regulatory approaches. The EPA, as mentioned above, is also reported to be in discussions with interested industry groups regarding the possibility of a National Aerosol Coatings Rule that would be similar to the CARB reactivity-based rule (PCA Services, 2006)

4.3.3.4.2 Collaborative Efforts for Regional and National Applications

In 1998, the RRWG was formed by the EPA, NARSTO (previously called the North American Research Strategy on Tropospheric Ozone), and academic and industrial partners (NARSTO, 2006). The goal of this group is to coordinate the development of an improved scientific basis for reactivity-related policies, in particular for addressing questions inhibiting the design of ozone control strategies that could take advantage of the variations in reactivity among VOCs. This consortium invited members from

communities potentially impacted by reactivity-related regulatory actions so that concerns could be addressed as they arose and practical solutions would be proposed and evaluated.

4.3.3.4.3 Regional Modeling of Reactivity

Under the coordination of the RRWG, and taking advantage of recent advancements in numerical techniques and computational capacities, reactivity quantification metrics were recently evaluated on regional scales (Arunachalam *et al.*, 2003; Carter *et al.*, 2003; Hakami, 2003; Hakami *et al.*, 2004a; Hakami *et al.*, 2004b). The study described above was part of this integral program. Combined, these studies show that the relative ranking of MIR based reactivity metrics were fairly consistent with results from previous modeling studies, even over these large regional domains. In a final evaluation report to the RRWG, R.G. Derwent summarized that, "[t]aken together, these three studies have made a significant contribution to basic understanding of the likely role that reactivity considerations could play in ozone control strategies. These studies have shown that reactivity-based policies should work efficiently on both the urban and regional scales by reducing episodic peak ozone levels and by reducing the exceedances of the ozone air quality standards." (Derwent, 2004).

4.3.4 Conclusions

Reactivity weighting of VOC emissions for ozone control has very specific applications. Increased concentrations of tropospheric ozone are observed on urban, regional, and global scales (Fiore *et al.*, 2002b). NO_x reduction is ultimately required for ozone reduction; however anthropogenic VOC emission controls are effective in polluted, urban areas that are VOC limited. These areas are usually highly populated where elevated ozone concentrations have the greatest impacts on human health.

Accounting for reactivity in VOC reduction control strategies provides regulatory flexibility, which can decrease the costs of control, while maintaining or surpassing ozone reduction achievable through NO_x reduction alone. Participation of the scientific, regulated, and regulatory communities in designing these regulations promise to result in more efficient strategies and greater cooperation in compliance. A supplementary benefit of accounting for reactivity in emissions reduction requirements is the added incentive for better characterization of VOC emissions. Many compounds categorized as VOCs degrade health and the environment through mechanisms other than ozone formation. As the emissions profiles of sources become better known, the impact of individual compounds can be better tracked through epidemiology and environmental studies, and if harmful compounds are identified, controls can be more quickly and effectively applied to better characterized sources.

Recognition of the regional component and increasing global background concentrations of tropospheric ozone, along with an increased understanding of the widespread health impacts of related pollutants, clearly indicate the need for more chemically and spatially integrated approaches to air quality management and atmospheric maintenance and stewardship. Precursors to ozone contribute to other important pollutants, such as particulate matter and acid deposition, and some of the major sources of these precursors also contribute to pollution issues such as mercury deposition and climate change (Bergin *et al.*, 2005), providing co-benefits to many emissions control options. Our continually increasing understanding of atmospheric processes and the emissions and reactivity of VOC compounds enhances our ability to develop efficient and cost effective air quality management strategies.

REFERENCES

Arunachalam, S., R. Mathur, A. Holland, M. R. Lee, J. Donald Olerud and H. Jeffries (2003). Investigation of VOC Reactivity Assessment with Comprehensive Air Quality Modeling. Final Report. U.S. Environmental Protection Agency. GSA Contract # GS-35F-0067K, Task Order ID: 4TCG68022755.

Bergin, M., W. P. L. Carter, J. Milford, P. J. Ostrowski and A. G. Russell (1999a). Reactivity Assessments. Relative Reactivity Working Group. Available from: http://www.narsto.org/section.src?SID=10

Bergin, M. S. and J. B. Milford (2000). "Application of Bayesian Monte Carlo analysis to a Lagrangian photochemical air quality model." *Atmospheric Environment* **34**(5): 781-792.

Bergin, M. S., G. S. Noblet, K. Petrini, J. R. Dhieux, J. B. Milford and R. A. Harley (1999b). "Formal uncertainty analysis of a Lagrangian photochemical air pollution model." *Environmental Science & Technology* **33**(7): 1116-1126.

Bergin, M. S., A. G. Russell, W. P. L. Carter, B. Croes and J. H. Seinfeld (1998a). VOC Reactivity and Urban Ozone Control. In Encyclopedia of Environmental Analysis and Remediation. J. W. Sons. New York**:** 3355-3383.

Bergin, M. S., A. G. Russell and J. B. Milford (1998b). "Effects of chemical mechanism uncertainties on the reactivity quantification of volatile organic compounds using a three-dimensional air quality model." *Environmental Science & Technology* **32**(5): 694-703.

Bergin, M. S., A. G. Russell, Y. J. Yang, J. B. Milford, F. Kirchner and W. R. Stockwell (1996). Effects of Uncertainty in SAPRC90 Rate Constants and Selected Product Yields on Reactivity Adjustment Factors for Alternative Fuel Vehicle Emissions. Report to the National Renewable Energy Laboratory NREL/TP-425-7636. Golden, CO.

Bergin, M. S., J. J. West, T. J. Keating and A. G. Russell (2005). "Regional atmospheric pollution and transboundary air quality management." *Annual Review Of Environment And Resources* **30**: 1-37.

CARB (2000). Technical Support Document: Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products,and Proposed Tables of Maximum Incremental Reactivity (MIR)Values, and Proposed Amendments to Method 310, “Determination of Volatile Organic Compounds in Consumer Products”. State of California Air Resources Board. Available from: http://www.arb.ca.gov/regact/conspro/aerocoat/execsum.pdf

CARB (2004). California Air Resources Board (CARB). "Regulatory Documents for the California Consumer Products Regulation Relating to Aerosol Coating Products". http://www.arb.ca.gov/regact/conspro/aerocoat/aerocoat.htm (Accessed: Oct., 2006).

CARB (Apr 1992). Development and Evaluation of OzoneReactivity Scale for Low-Emission Vehicles and Clean Fuel Regulations. State of California Air Resources Board. Sacramento, CA.

CARB (Aug 1990). Proposed Regulations for Low-Emission Vehicles and Clean Fuels: Staff Report and Technical Support Document. State of California Air Resources Board. Sacramento, CA.

Carter, W. P. L. (1994). "Development of Ozone Reactivity Scales for Volatile Organic Compounds." *Journal of the Air and Waste Management Assoc.* **44**: 881-899.

Carter, W. P. L., G. Tonnesen and G. Yarwood (2003). Investigation of VOC reactivity effects using existing regional air quality models. Final Report. American Chemistry Council. Contract SC-20.0-UCR-VOC-RRWG.

Chameides, W. L., R. W. Lindsay, J. Richardson and C. S. Kiang (1988). "The Role of Biogenic Hydrocarbons in Urban Photochemical Smog: Atlanta as a Case Study." *Science* **241**(4872): 1473-1475.

Derwent, R. G. (2004). Evaluation and characterisation of reactivity metrics. Report to US Environmental Protection Agency, Order No. 4D-5844-NATX. Research Triangle Park, NC.

EPA (2003). U.S. Environmental Protection Agency, Office of Air and Radiation. 40 CFR Part 51. . "Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans". Available from: http://www.epa.gov/ttncaaa1/t1/memoranda/27601interimguidvoc.pdf (Accessed Oct., 2006).

EPA. (2005). U.S. Environmental Protection Agency. Federal Registry. Revisions to the California State Implementation Plan and Revision to the Definition of Volatile Organic Compounds (VOC)—Removal of VOC Exemptions for California's Aerosol Coating Products Reactivity-Based Regulation. 70, No. 176, 53930.

Fine, J., L. Vuilleumier, S. Reynolds, P. Roth and N. Brown (2003). "Evaluating uncertainties in regional photochemicalair quality modeling." *Annual Review of Environment and Resources* **28**: 59-106.

Fiore, A. M., D. J. Jacob, R. M. Bey, Yantosca, B. D. Field, A. C. Fusco and J. G. Wilkinson (2002). " Background ozone over the United States in summer: Origin, trend, and contribution to pollution episodes." *Journal of Geophysical Research-Atmospheres* **107**(D15): 4275.

Hakami, A., M. S. Bergin and A. G. Russell (2004a). "Ozone formation potential of organic compounds in the eastern United States: A comparison of episodes, inventories, and domains." *Environmental Science & Technology* **38**(24): 6748-6759.

Hakami, A., Bergin, M. S., Russell, A. G. (2003). Assessment of the ozone and aerosol formation potentials (reactivities) of organic compounds over the eastern United States. Report to the American Chemistry Council and California Air resources Board.

Hakami, A., R. A. Harley, J. B. Milford, M. T. Odman and A. G. Russell (2004b). "Regional, three-dimensional assessment of the ozone formation potential of organic compounds." *Atmospheric Environment* **38**(1): 121-134.

Khan, M., Y. J. Yang and A. G. Russell (1999). "Photochemical reactivities of common solvents: comparison between urban and regional domains." *Atmospheric Environment* **33**(7): 1085-1092.

Martien, P. T., R. A. Harley, J. B. Milford and A. G. Russell (2003). "Evaluation of incremental reactivity and its uncertainty in Southern California." *Environmental Science & Technology* **37**(8): 1598-1608.

McNair, L., A. Russell and M. T. Odman (1992). "Airshed Calculation of the Sensitivity of Pollutant Formation to Organic-Compound Classes and Oxygenates Associated with Alternative Fuels." *Journal of the Air & Waste Management Association* **42**(2): 174-178.

Milford, J. B., D. Gao, A. G. Russell and G. J. McRae (1992). "Use of Sensitivity Analysis to Compare Chemical Mechanisms for Air-Quality Modeling." *Environmental Science & Technology* **26**(6): 1179-1189.

NARSTO (2006). Previously the North American Research Strategy on Tropospheric Ozone. "NARSTO Activities: VOC Reactivity". Available from: http://www.narsto.org/section.src?SID=10 (Accessed: Oct., 2006).

NRC (1991). Rethinking the Ozone Problem in Urban and Regional Air Pollution. Washington, D.C., National Research Council, National Academy Press.

Oreskes, N., K. Shraderfrechette and K. Belitz (1994). "Verification, Validation, and Confirmation of Numerical-Models in the Earth-Sciences." *Science* **263**(5147): 641-646.

PCA Services, I. (2006). Potential Approach to Aerosol Coatings Product Regulations in Texas, Project H-54. Available from: http://files.harc.edu/Projects/AirQuality/Projects/H054/H054AerosolCoatings.pdf#search=%22CARB%20aerosol%20coating%20reactivity%22

Russell, A. and R. Dennis (2000). "NARSTO critical review of photochemical models and modeling." *Atmospheric Environment* **34**(12-14): 2283-2324.

Russell, A., J. Milford, M. S. Bergin, S. McBride, L. McNair, Y. Yang, W. R. Stockwell and B. Croes (1995). "Urban Ozone Control and Atmospheric Reactivity of Organic Gases." *Science* **269**(5223): 491-495.

TCEQ (2006a). Texas Commission on Environmental Quality. "HRVOC Emissions Cap and Trade Program". http://www.tceq.state.tx.us/permitting/air/banking/hrvoc_ept_prog.html (Accessed Oct, 2006).

TCEQ (2006b). Texas Commision on Environmental Quality. "SIP Revision: Houston-Galveston-Brazoria; Ch. 101 and Ch. 115 Rules. Also, Executive Summary." http://www.tceq.state.tx.us/implementation/air/sip/dec2004hgb_mcr.html (Accessed: Oct., 2006).

Tonnesen, G., J. Olaguer, M. Bergin, T. Russell, A. Hanna, P. Makar, D. Derwent and Z. Wang (1998). Air Quality Models. Relative Reactivity Working Group. http://www.narsto.org/section.src?SID=10

Yang, Y. J., W. R. Stockwell and J. B. Milford (1995). "Uncertainties in Incremental Reactivities of Volatile Organic-Compounds." *Environmental Science & Technology* **29**(5): 1336-1345.

CHAPTER 5

REGIONAL ATMOSPHERIC POLLUTION AND TRANSBOUNDARY AIR QUALITY MANAGEMENT

(Michelle S. Bergin, J. Jason West, Terry J. Keating, and Armistead G. Russell.*)
Annual Review of Environment and Resources, 2005, 30:1-37.*)

Abstract

The regional nature of several important air pollutants, which include acids, ozone, particulate matter, mercury, and persistent organics, is widely recognized by researchers and decision makers. Such pollutants are transported regionally over scales from about 100 to a few 1000s of kilometers, large enough to cross state, provincial, national, and even continental boundaries. Managing these regional pollutants requires overcoming political, economic, and cultural differences to establish cooperation between multiple jurisdictions, and it requires recognition of the linkages between pollutants and of impacts at different geographic scales. Here, regional dynamics of the pollutants are discussed, addressing them individually and as a tightly linked physical and chemical system. Collaborative efforts to characterize and manage regional pollution are presented, along with potential directions for future efforts.

5.1 Regional Air Pollution

Current estimates are that a quarter of the world's population is exposed to unhealthy concentrations of ambient air pollutants (WHO, 2004), with nearly 6.4 million years of healthy life lost owing to long-term exposure to ambient particulate matter alone (WHO, 2003). Research results indicate further harmful health effects from ozone, airborne metals (e.g., mercury), and organics (e.g., benzene, dioxins). Additionally, air pollution damages crops, built structures such as buildings and historic monuments, ecosystems, and wildlife. Outdoor air pollution largely results from the combustion of fossil fuels for transportation, power, and other human activities (WHO, 2004), although natural sources play important roles in determining the ultimate impact of those anthropogenic emissions. Without further actions to control emissions, air pollution problems will only worsen as populations and fossil-fuel combustion increase.

Although stratospheric ozone depletion and climate change have been identified as global issues, most air pollution has historically been viewed and treated as local or urban scale. Now both the scientific and political communities increasingly recognize that several important air pollutants have regional distributions. Attention has shifted toward regional air pollution for a number of reasons. First, shifting demographic and development growth patterns decentralized industrial and transportation-related emission sources over regional scales. Second, past urban-scale air quality management has effectively addressed some of the most apparent urban problems [such as smoke, lead, CO, and total suspended particulate (TSP)], allowing regional problems to come to the forefront. Similarly, control of urban emissions has often made the regional contribution a growing fraction of the total pollutant concentrations in an urban area. Third, management efforts have found that some controls, such as those on vehicles, are best applied over larger areas because of economies of scale and because such sources move between political jurisdictions. Finally, scientific research, in part through ground-based measurements, satellite observations, and modeling studies, has shown that urban

pollutants such as ozone and particulate matter are transported long distances, and research has highlighted the importance of the impacts of those pollutants on human health and ecosystems. A recent report from the National Research Council in the United States listed pollutant transport across multistate regions, national boundaries, and continents as one of the seven major air quality challenges facing the United States in the coming decades (NRC, 2004), and this challenge is important to many other nations as well.

Regional-scale air pollution is defined in this review as being on the order of 100 to a few 1000s of kilometers. Over this scale, geographic patterns of transport are dependent on the pollutant considered, the location of emissions, and meteorology, which may themselves be affected by changes in topography. This scale is often large enough to include multiple political jurisdictions, i.e., states, provinces, or nations, and the geographic patterns of pollutants often do not coincide with the boundaries of political jurisdictions. Consequently, impacts of air pollution in one political jurisdiction may be caused, in part, by emissions from another jurisdiction, making cooperation necessary to achieve pollution control.

In this review, we first present an introduction to regional atmospheric transport and chemistry as well as to the impacts, chemistry, and physics of several significant regional air pollutants of current and historical interest. We present each of these pollutants individually [acid deposition, tropospheric ozone, particulate matter, mercury, and persistent organic pollutants (POPs)], then discuss some of their important linkages with regional climate change and with each other. After providing this scientific background, we describe efforts to cooperatively characterize and manage these regional pollution problems and discuss potential directions for future policy efforts. Although there is still much to be learned about the regional nature of different air pollutants, our current scientific understanding recognizes that transboundary air pollution is common and suggests that future management efforts must recognize both the linkages across

geographic scales and linkages between pollutants (NRC, 2004), making political cooperation necessary.

5.2 General Characteristics of Regional Atmospheric Transport and Chemistry

Air pollutants are broadly categorized as either primary or secondary. Primary pollutants are directly emitted, such as inorganic carbon particulates (e.g., diesel soot). Secondary pollutants, such as tropospheric ozone and much of the fine particulate mass, are formed through chemical reactions in the atmosphere. Primary pollutants can be managed directly by reducing their emissions, although sources may be hard to identify or reduce. Management of secondary pollutants can be more complex because their relationships to emission sources may not be readily apparent and response to emission reductions may not be proportional.

Whether a pollutant has a regional impact is determined by its rate and method of emission and/or formation, method of transport, and removal and/or destruction processes—many of which are bound by the governing processes of the atmosphere and natural emission patterns. The atmosphere is far from equilibrium, and its chemical nature, transport properties, and other characteristics all play a role in the fate of air pollutants. In particular, the atmosphere is both oxidative and turbulent, and these two characteristics dominate the evolution of pollutants after emission.

In a regional context, pollutant transport occurs in the lower atmosphere, or troposphere, which is approximately 10 km thick. The troposphere includes the planetary boundary layer (PBL) and the free troposphere above it. The PBL is the most directly influenced by warming and cooling of the earth's surface, and its thickness varies generally between a few hundred to a couple thousand meters during the day. Most regional air pollutants are contained in this boundary layer. Within the PBL is the mixed layer, which is the region where the most rapid turbulent mixing occurs.

Turbulence in the mixed layer is caused by ground-layer heating and mechanical forcing, which drives vertical transport. Vertical transport and mixing has a large effect on the ultimate distance pollution is carried and on the dilution and chemical progression of the initial air parcel. Ground-layer heating warms air parcels next to the surface, causing them to rise, whereas colder air parcels from above (from adiabatic expansion) fall, creating an unstable atmosphere with thermal eddies, which efficiently disperse pollutants throughout the mixed layer. This mixing can dilute ground-level emissions upward and fumigate elevated plumes, e.g., from power plants, downward. On a sunny day, thermal mixing dominates vertical pollutant dispersion, with pollutants diffused up to hundreds of meters in a few minutes. On less sunny days, or at night, mixing still occurs owing to mechanical turbulence generated by the wind, which interacts with a rough surface, although this process is slower. When there is little or no sunlight, the atmosphere can become stable as cooling at the earth's surface traps cold air below warmer air. In such cases, mechanically generated turbulence can also be inhibited, leading to high concentrations of ground-level pollutants trapped very near the surface (NRC, 2003).

Horizontal transport is dominated by advection, generally following customary local and regionally seasonal wind currents. One estimate suggests that the climatologically averaged mean transport velocity is around 400 km per day, although this depends on episodic meteorology and can vary from a few tens of kilometers to about 1000 km. Strong winds can spread emissions and pollutants over a wide region, transporting persistent pollutants, increasing background concentrations, and causing occasional severe pollution episodes (i.e., dust storms). However, many of the more severe pollution episodes occur when the air is more stagnant, exacerbating the impact of local sources.

Transport and pollution patterns are influenced by physical changes on the earth's surface, such as land-ocean interfaces, mountain ranges, and variations in surface terrain.

Pollutant distribution is also affected strongly by the location of emission sources, including the dispersion of mega-city emissions from highly industrialized regions, and the geographical distribution of land-use changes that affect both anthropogenic and natural emissions (such as forest versus desert emissions).

Emissions result from natural sources, such as soil, plants, volcanoes, and lightning, and from anthropogenic sources, such as power plants, industrial processes, cars, and farm equipment. These sources can be affected by meteorological and human activity pattern changes (e.g., daily, weekly, seasonal) and other variables, including the altitude at which the source operates. For example, mobile sources often have higher organic emissions at high altitudes. Once precursors or pollutants are emitted, the distances they travel are largely governed by the rates of chemical reaction and deposition processes.

Oxidation (such as the transformation of NO to NO2) often initiates the chemical reactions of emissions that lead to secondary pollutant formation (Prinn, 2003). In fact, oxidation by the hydroxyl radical (HO•) is key to the formation and fate of many regional pollutants (as described below). Radiative energy from the sun also facilitates various chemical reactions and alters the rates, spatial distributions, and chemistry of many emissions (e.g., biogenic and evaporative emissions), so pollution follows daily, seasonal, and latitudinal patterns. The emission sources and chemistries of many regional pollutants are closely linked by these factors.

Secondary formation can occur rapidly or over a long period of time depending on the chemical pathways, the presence of other precursor species or catalysts, and whether meteorological conditions are conducive to production. Major chemical pathways for secondary pollutant formation include oxidation, photochemistry (reactions requiring energy from the sun), and heterogeneous chemistry (generally occurring on or in liquid droplets in clouds or fog). These processes can occur individually or in conjunction with each other. Chemical transformations can involve the formation of

intermediate species, which may be stable under some conditions and then react under other meteorological conditions or in the presence of other chemical species. The formation of intermediate species can contribute to the long-range transport of pollution.

Together with the chemical destruction of pollutants, deposition to the earth's surface determines the lifetime of pollutants and the extent of their transport. Deposition may occur with precipitation (i.e., wet deposition) or without (i.e., dry deposition). In dry deposition, gases and small particles turbulently diffuse in the mixed layer to very near the surface, where Brownian diffusion and residual turbulence move the pollutants into contact with surfaces to which they can physically adhere (i.e., particles) or be consumed chemically or bonded (i.e., gases). Depending on variables, such as the pollutant species (if a gas), the particle size (if an aerosol), the surface, and the prevailing meteorology, the rate of deposition can vary widely. For example, nonreactive gases, like CO, have a deposition velocity on the order of 0.0003 m/s or less, leading to a characteristic lifetime due to deposition of weeks or more. Conversely, reactive gases, like nitric acid, can have a deposition velocity as high as 0.04 m/s, leading to a lifetime of hours (Seinfeld and Pandis, 1998).

Wet deposition occurs when the pollutant becomes associated with a droplet (fog, rain, cloud, or snow) that deposits to a surface. Pollutant gases and particles diffuse to the droplet surface and are absorbed, or particles impact a droplet. In some cases, the pollutant actually seeds the formation of the droplet (serves as a nucleation site), affecting climate as discussed further below. Timescales for wet deposition are highly variable.

5.3 Regional Air Pollutants and Effects

The previous section discussed general processes that affect the geographic distributions of pollutants. However, each pollutant has unique impacts, causes, and chemistry. This section discusses individual regional-scale air pollutants and their effects, including (a) acid deposition, which destroys or damages aquatic and terrestrial

ecosystems and manufactured materials, (b) tropospheric ozone, which harms the health of humans, wildlife, crops, and ecosystems, and is a greenhouse gas, (c) particulate matter, which also harms health, degrades visibility, and changes precipitation and temperature patterns, (d) mercury, which is toxic to humans, plants, and animals, and bioaccumulates in the food chain, and (e) POPs, which are also toxic, bioaccumulate, and remain in the environment for many years. Regional climate change is also discussed, which both impacts and is impacted by regional air pollution.

5.3.1 Acid Deposition

Deposition of acidic compounds is one of the best-known regional air pollution problems and, as discussed below, has been the focus of several transboundary agreements. Acids are deposited to the earth's surface through both wet and dry processes. Acid rain in a polluted area often has a pH in the range of 3 to 4, and even lower values have been measured (AMS, 2003). For comparison, the natural pH of precipitation is around 5.6 (slightly acidic) owing to reactions of carbon dioxide with water in the atmosphere (Seinfeld and Pandis, 1998). Most aquatic insects, algae, and plankton cannot tolerate water with a pH below 5.0. These organisms are at the base of the food chain, and their survival affects the survival of all other aquatic organisms. A pH below 5.0 can also result in reproductive failures in fish and amphibians (AMS, 2003). Acid deposition also harms terrestrial ecosystems and manufactured surfaces and materials, including historic buildings and monuments (EPA, 2002a).

Harmful effects are caused directly by acidification and/or indirectly by the addition of poisonous metals, such as aluminum and mercury, that are mobilized when acidified runoff leaches the metals from soils and clay. A body of water can be "shocked" by a large acid load from snowmelt runoff in the spring. Effects on human health are uncertain, but there are likely effects from ingesting fish that have bioaccumulated

leached mercury and/or aluminum, and effects are known to occur from respiring related acidic aerosol particles.

The natural pH of water bodies and soils varies considerably depending on the soil composition of a watershed, including its buffering capacity. These differences explain why some areas are highly susceptible to damage from acid deposition (e.g., lakes in the northeastern United States and the Black Forest in Germany), whereas other areas, such as those with soils rich in lime, are relatively resistant. Additionally, meteorology and emission patterns cause some areas to experience much higher concentrations of deposited acids than others. Extensive damage from acid deposition has been found in eastern North America, northern Europe, Japan, China, and Southeast Asia (Figure 5.1). These patterns of deposition clearly cross political boundaries.

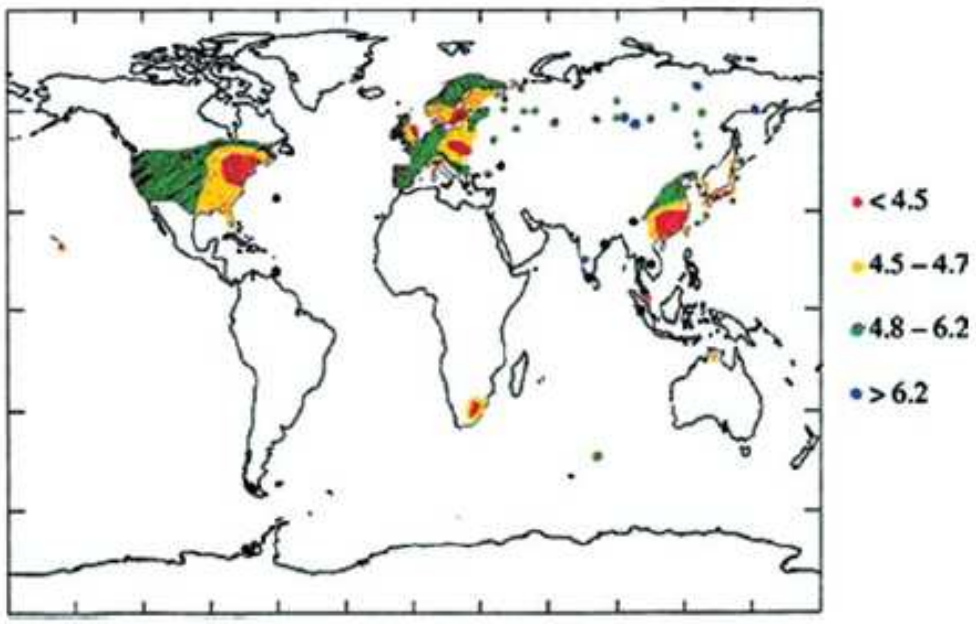


Figure 5.1. Observed values of volume-weighted annual average pH of precipitation. Reproduced with permission from (Rodhe *et al.*, 2002).

The vast majority of acid deposition pollution is caused by emissions of sulfur dioxide (SO_2) and oxides of nitrogen (NO and NO_2, together referred to as NO_x), which are primarily from fossil-fuel combustion in power plants and vehicles (AMS, 2003). High emissions of both precursors are in southeastern Asia, eastern North America, and western Europe (Figures 5.2 and 5.3), although biomass burning, which contributes about one third of the global NOx, is the dominant source of anthropogenic NO_x in the Southern Hemisphere (Seinfeld and Pandis, 1998). Fossil-fuel combustion is the overwhelming source of SO_2 emissions (Seinfeld and Pandis, 1998). There are also natural sources of these precursors, such as volcanoes (NO_x and SO_2) and vegetation, soil, and lightning (NO_x). In addition to acid deposition, atmospheric nitrogen pollution (including both oxidized and reduced forms) is responsible for impacts on human health, visibility, crop damage, and regional eutrophication of soils and waters, as well as on climate change and stratospheric ozone depletion (e.g., N_2O emissions) (Driscoll *et al.*, 2003; Erisman *et al.*, 2003; Galloway *et al.*, 2003). In a cycle termed the nitrogen "cascade," an atom of emitted nitrogen can participate in many pollution effects before being immobilized or converted back to a benign form (e.g., N_2). Nitrogen emissions from transportation, energy generation, and industrial and agricultural activities are found to contribute significantly to the total nitrogen pollution cascade (Driscoll *et al.*, 2003; Erisman *et al.*, 2003).

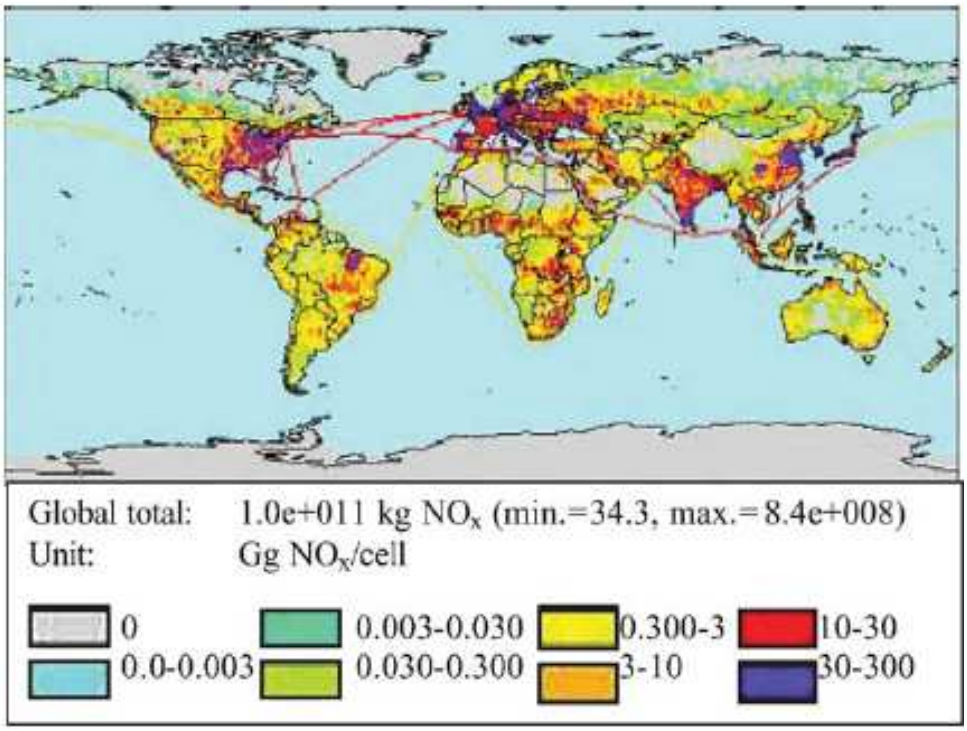


Figure 5.2. NO_x from anthropogenic sources in 1995. Reproduced with permission from (RIVM, 1995).

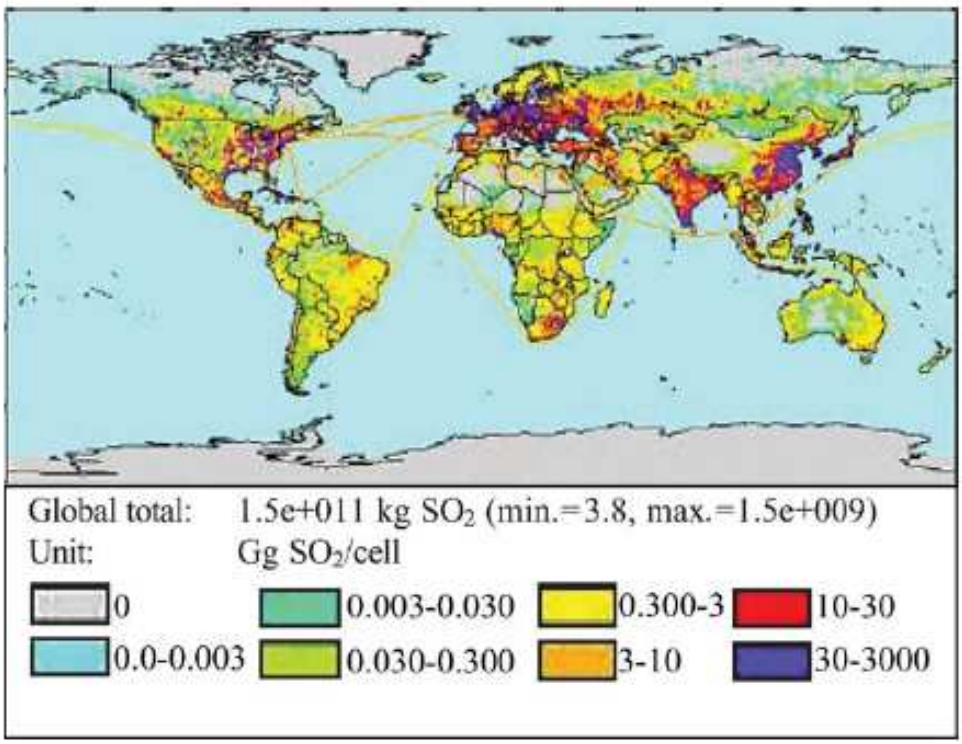


Figure 5.3. SO_2 from anthropogenic sources in 1995. Reproduced with permission from (RIVM, 1995).

Reactions of SO_2 with peroxides (e.g., H_2O_2) in clouds or with HO• in air lead to sulfuric acid (H_2SO_4) (Figure 5.4). Sulfuric acid is highly soluble, so it is incorporated by clouds, fog, and raindrops. NO_2 is also oxidized by HO• and by nighttime heterogeneous reactions involving ozone, resulting in the formation of nitric acid (HNO_3). Nitric acid is easily deposited to surfaces through both wet and dry processes. The HO• and HO_2•, which cycle between each other, are central to the chemical transformation of virtually all species (Prinn, 2003). HO• is formed primarily from the photolysis of ozone followed by reaction with water.

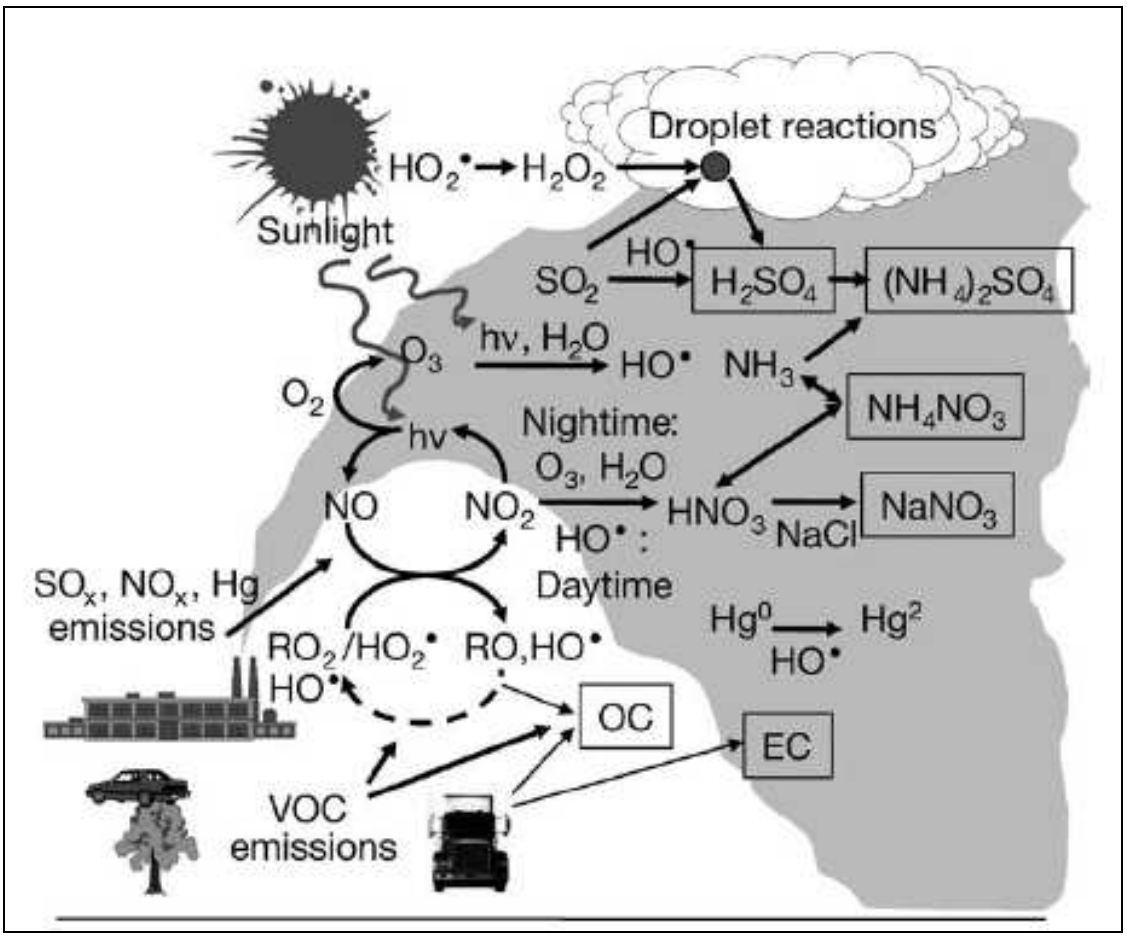


Figure 5.4. Schematic of the unified chemistry of regional ozone, particulate matter, acids, and mercury. Particulate phase species are boxed.

In general, NO_x is converted to nitric acid within a few days or less after being emitted, and SO_2 is converted to sulfuric acid within several days, suggesting that mean transport distances of SO_2, NO_x, and their oxidation products are 200 to 1200 km before deposition (Seinfeld and Pandis, 1998; Jacobson, 2002). In addition to direct transport, NO_x can form semistable compounds (organonitrates) that can travel hundreds to thousands of kilometers within the cooler regions of the troposphere before converting back to NO_x and then to nitric acid.

In the 1950s and 1960s, the regional nature of acid deposition became apparent when a relationship was demonstrated between emissions of sulfur in continental Europe and acidification in Scandinavian lakes (Jacobson, 2002). Cooperative monitoring and modeling studies of regional acid deposition in Europe began in the early 1970s under the auspices of the Organization for Economic Cooperation and Development and led to the 1979 Convention on Long-Range Transboundary Air Pollution (discussed in more detail below). Awareness of the regional nature of acid deposition in North America followed and, in the United States, led to the formation of the National Atmospheric Deposition Program in 1978 and the National Acid Precipitation Assessment Program in 1981 (Cowling, 1982). Recognition of the large-scale nature of acid precipitation in eastern North America led to the development of a regional emission trading program in the United States (discussed below) and to emission reduction commitments contained in the 1991 Canada-United States Air Quality Agreement. Regional acid deposition was recognized in East Asia in the early 1990s, and eventually led to the creation of the Acid Deposition Monitoring Network in East Asia (EANET) in 1998 (http://www.adorc.gr.jp/).

5.3.2 Tropospheric Ozone

Ozone (O_3) is a highly reactive state of oxygen, and concentrations between 10 and 40 parts per billion (ppb) occur naturally in a clean troposphere through both

stratospheric injection and chemical reactions of natural emissions in the troposphere. Ozone concentrations in polluted urban areas reach between 100 and 400 ppb (Seinfeld and Pandis, 1998). Tropospheric ozone was first recognized as an urban air pollution problem, notably in Los Angeles in the 1940s, and for decades was perceived and treated as an urban-scale problem. During the 1980s, measurement and modeling studies demonstrated the more regional nature of ozone pollution, in part as a result of the success in reducing extreme urban ozone episodes.

Anthropogenic ozone is responsible for damage to human health, crops, natural vegetation, and wildlife, and it is a potent greenhouse gas that contributes to global climate change (NRC, 1991; EPA, 1996; IPCC, 2001). Ozone causes both acute and chronic health problems, especially related to lung functions, asthma, and pulmonary infection (Bell *et al.*, 2004), as well as other health end points including daily hospital admissions (Levy *et al.*, 2001)(16). Ozone may also cause chronic health effects, although no link with long-term mortality has been demonstrated (Levy *et al.*, 2001; Pope *et al.*, 2002). Although people with preexisting respiratory disease and children are most sensitive to ozone damage (CDCP, 1995), much evidence indicates that ozone can adversely affect the respiratory systems of any individual depending on the conditions of exposure (Horvath and McKee, 1994). In 2002, over 50% of the U.S. population lived in counties where monitored air pollution was found to exceed the human health based National Ambient Air Quality Standards (NAAQS); the vast majority of this pollution was due to ozone and particulate matter (Census, 2002; EPA, 2002a). Many urban areas outside of the United States also often experience ozone levels far exceeding the current U.S. NAAQS, and other nations have set even lower concentration standards.

In addition to human health impacts, air pollution affects agricultural production (Mauzerall and Wang, 2001), accounting for an estimated several billion dollar crop loss every year in the United States alone (Tingey *et al.*, 1994). Estimates are that 10% to 35% of the world's grain production occurs in regions where ozone pollution likely

reduces crop yields (Chameides *et al.*, 1994). Ozone may also cause short- and long-term damage to the growth of forest trees (McLaughlin and Downing, 1995) and alters the biogenic hydrocarbon emissions of vegetation. In addition, research is examining ozone effects on sensitive wildlife populations. Even accounting for planned reductions in precursors from some regions, concentrations of ozone are predicted to increase over the next decades (IPCC, 2001; Derwent *et al.*, 2002). As discussed below, tropospheric ozone also impacts climate.

Although a small amount of ozone is transported from the stratosphere to the troposphere, the only significant process that forms ozone in the lower atmosphere involves reactions between volatile organic compounds (VOCs) and NO_2 in the presence of sunlight (Figure 5.4). Photolysis of NO_2 is followed by the rapid reaction of the released oxygen atom with O_2, which is quickly reversed by the reaction of O_3 with NO. With no other removal process for NO (and most NO_x is emitted as NO), reactions with the released NO would rapidly deplete ozone, and there would be no net ozone formation—as is the case at night with near-surface NO_x emissions. VOCs provide the energy needed to oxidize NO to NO_2, with some reactive VOCs actually cycling NO to NO_2 many, many times over. Ozone removal is largely dependent on photolysis reactions, kinetic reactions, and deposition (Seinfeld and Pandis, 1998). Photolytic loss depends on water vapor concentration, so it is highest at low altitudes in the tropics, which have high radiation and high humidity (Jacobson, 2002). Loss to deposition takes a few days over land, and longer over water. Ozone and its precursors can be transported over large regions (Derwent *et al.*, 2002), making it difficult or even impossible for some areas to manage their own concentrations through local emission controls (Bergin *et al.*, 2006c).

As noted above, NO_x emissions, which lead to increased ozone concentrations, are mainly produced during fossil-fuel combustion in the Northern Hemisphere and biomass burning in the Southern Hemisphere (Figure 5.2). Globally, most VOC

emissions are biogenic, emitted by plants and trees, although anthropogenic VOCs in heavily polluted areas are instrumental in the formation of high ozone concentrations. Anthropogenic VOCs arise from many sources, including exhaust and evaporative emissions from vehicles, solvents, surface coating activities, food cooking, and dry cleaning. There are hundreds of different compounds classified as VOCs, and their ozone formation potentials (termed reactivity) vary widely (Carter, 1994; Bergin *et al.*, 1998a).

In urban areas, ozone formation may be limited by emissions of either NO_x or VOCs, depending mainly on the relative concentrations of the two. Because ozone formation requires time, and NO emissions initially decrease ozone, peak ozone concentrations are often observed downwind of large emission sources (i.e., industrial or urban areas), and correspondingly, emission reductions may benefit downwind areas much more than local areas (Figure 5.5). Because NO_x is relatively short lived in the atmosphere, and because of the availability of (mainly biogenic) VOCs in many rural regions, ozone formation on a regional scale is generally limited by the availability of NO_x (NRC, 1991).

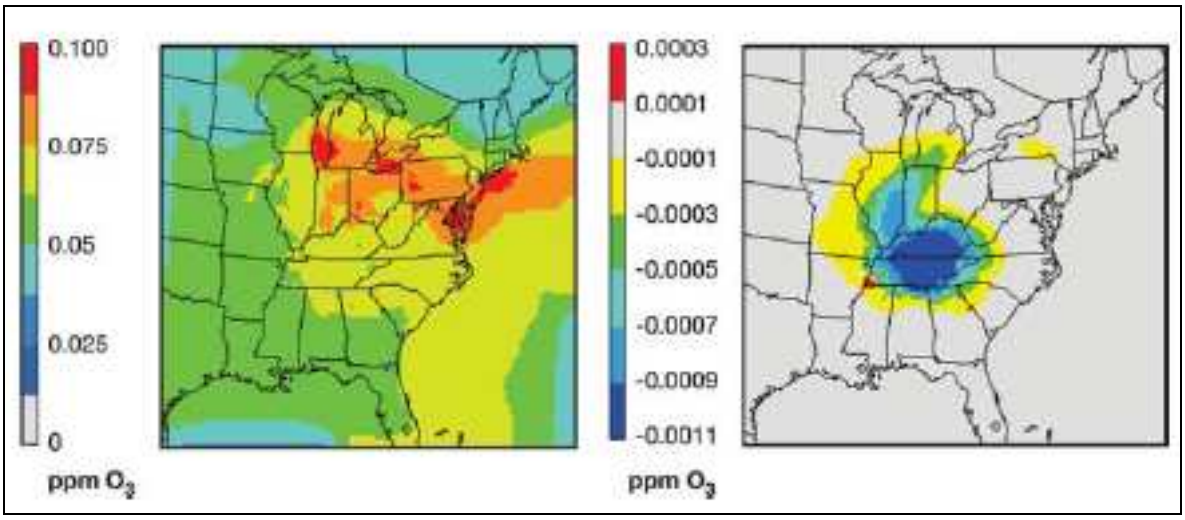


Figure 5.5. Regional ozone and sensitivity to emissions. (a) Simulated one-hour averaged ozone concentration and (b) its sensitivity to a 30% reduction in surface NO_x emissions from Tennessee (Bergin *et al.*, 2006b).

In the United States, the regional nature of ozone formation was described as a "river of ozone" flowing along the east coast of the United States from the District of Columbia to New England (Wolff and Lioy, 1980). Through the 1980s and early 1990s, a number of monitoring and modeling studies were performed to examine the regional nature of ozone, including the San Joaquin Valley Air Quality Study (Ranzieri and Thullier, 1991), the Lake Michigan Ozone Study (Dye *et al.*, 1995), the Regional Ozone Modeling for Northeast Transport, and the Southern Oxidant Study (SOS) (Chameides and Cowling, 1995a). The SOS demonstrated that the river analogy used to describe regionality in the Northeast was not applicable in the Southeast. Instead, the SOS found that urban areas and power plants tended to add fresh emissions to a ubiquitous sea of VOCs, leading to widespread and simultaneous formation of ozone across the Southeast and creating a "rising tide of ozone" (Chameides and Cowling, 1995a). These ozone studies formed the basis for regional management strategies implemented in the late 1990s, as described further below. Some recent modeling studies examined the sensitivity of ozone in 19 individual U.S. states to emissions from other states to support policy decisions for air pollution control (Odman, 2002a; Bergin *et al.*, 2006c) and to evaluate cost-optimized emission reduction strategies (Shih *et al.*, 2003). Ozone concentrations in most states were found to be sensitive to emissions from other states (Figure 5.5).

Europe also began addressing ozone as a regional problem during the 1980s and 1990s. Cooperative research funded through the European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe (EUROTRAC) made significant contributions to understanding tropospheric ozone (Borrell *et al.*, 1997).

More recently, the potential for intercontinental ozone transport was demonstrated first by monitoring studies of the export of ozone from the east coast of North America (Parrish *et al.*, 1993) and Asia (Chameides *et al.*, 1999; Huebert *et al.*, 2003; Jacob *et al.*, 2003) and by modeling studies of trans-Atlantic (Li *et al.*, 2002; Derwent *et al.*, 2004)

and trans-Pacific transport (Jacob *et al.*, 1999; Yienger *et al.*, 2000). Historical measurements and modeling studies further suggest that anthropogenic NO_x emissions continue to increase global tropospheric ozone concentrations (Fiore *et al.*, 2002b; Prather *et al.*, 2003), thereby raising the background upon which urban and regional concentrations build.

5.3.3 Particulate Matter

Ambient aerosols (particulate matter) are chemically complex, dynamic mixtures of solids and liquids suspended in the atmosphere. Particulate matter is harmful to human and environmental health, degrades visibility, damages built structures, and alters climate. Some of the health impacts were recognized early (Jacobson, 2002), especially in highly polluted cities. Most regulations initially focused on controlling the mass of total suspended particulate (TSP). Restrictions could not be more specific because particles can rapidly change in both size and chemical composition as humidity, temperature, and other surrounding ambient concentrations change, making the aerosol composition difficult to sample and characterize.

As technical capabilities advanced, urban aerosols were found generally to form a trimodal lognormal size distribution in the atmosphere (by mass). The smallest mode, the nuclei mode, is composed of particles with aerodynamic diameters (Dp) less than about 0.1 μm (ultrafines). The accumulation mode is $0.1 < Dp < 2$ μm, and the coarse mode is $Dp > 2$ μm. The nuclei and accumulation modes are called fine particles.

Regulations soon targeted coarse particles (PM_{10}—particles which have $Dp < 10$ μm), rather than TSP. Currently, many regulations target particles with $Dp < 2.5$ μm ($PM_{2.5}$). Smaller particles have been emphasized in regulations for several reasons. First, smaller particles are more efficient at penetrating deep in the lungs, although there is evidence that particles in the 2.5 to 10 μm range also have health impacts (EPA, 2004a).

Larger particles also settle out rapidly, reducing their range of impact, and they have a smaller impact on visibility per unit mass.

Fine particulate matter (alone or in combination with other air pollutants) has been shown to cause a large number of adverse health effects, including premature death (EPA, 2002b; Pope, 2004) and an estimated global loss of nearly 6.4 million years of healthy life due to long-term exposure (WHO, 2003). Evidence of premature mortality comes from both daily time series studies (Stieb *et al.*, 2003) and long-term cohort studies that suggest particulate matter causes chronic health effects (Pope *et al.*, 2002). Exposure to larger particles is primarily associated with aggravation of respiratory conditions, such as asthma, and with premature death (Kaiser, 2000; EPA, 2002a).A threshold has not been identified under which particulate matter has no adverse health effects (WHO, 2004). Some recent studies indicate that the ultrafine particles may also be pivotal in health and environmental impacts (Guodong, 2004; Pekkanen and Kulmala, 2004); however the effects are difficult to assess because the methods and tools needed have not yet been fully developed and are not widely available (Guodong, 2004). Research is now also addressing whether the chemical composition of particles, in addition to size, affects health (Kaiser, 2000).

In addition to human health effects, soils, plants, water, and materials can also be damaged when particles deposit on them. The inorganic fraction of fine particulate matter, particularly sulfate, is responsible for much of the acid deposited and thus causes most of the impacts discussed above. Fine particulates are the most efficient size for scattering light in the atmosphere, causing large degradation of visibility and altering climate. In many parts of the United States, visual range has been reduced 70% from natural conditions by air pollution. The average visual range in eastern parks has decreased from 90 miles to 15–25 miles, and in western parks from 140 miles to 35–90 miles (EPA, 2004e). Light-scattering properties of aerosols, their effects on clouds, and

light-absorbing properties of some aerosols (i.e., elemental carbon) alter global and regional climate, as discussed below in the Regional Climate Change section.

Many of these aerosol effects depend on particle size, which is the result of many variables such as particle sources (both primary and secondary), the chemical composition of the local atmosphere, and meteorology. Particles of given sizes have differing emission, formation, and removal processes. Fine particles are both directly emitted into the atmosphere (by combustion processes) and formed in the atmosphere through secondary processes, such as condensation and heterogeneous chemical reactions (Figure 5.4). Coarse particles are generally primary (emitted) solids such as crustal materials (e.g., wind-blown dust), sea salt, pollen, and organic detritus, as well as fugitive dust from agricultural activities, unpaved roads, and industries.

Coarse particles tend to deposit rapidly through sedimentation, with atmospheric lifetimes of minutes to days, usually resulting in transport of less than tens of kilometers (Seinfeld and Pandis, 1998) and in local impacts. However, large dust storms and biomass burning events can carry coarse (and fine) particles very long distances (as discussed further below). Although dry deposition can also be important (Brasseur *et al.*, 1999), accumulation mode particles (fine particulate matter) are removed primarily by wet deposition (both in-cloud and below-cloud scavenging) and thus have atmospheric lifetimes of days to weeks, resulting in potential travel distances of hundreds to thousands of kilometers (Seinfeld and Pandis, 1998). Particles in the nuclei mode grow into the accumulation mode by coagulation and condensation. For these reasons, fine particulates are dominant in most regional-scale aerosol pollution events. In addition to size, hygroscopic properties of the aerosol (which depend on chemical composition) also determine travel distance.

Regional aerosol pollution patterns depend on the particle type and regional meteorology and topography. Regional and intercontinental aerosol pollution can be caused by transport of urban particles, biomass burning, and dust storms, which are

mostly natural but can be increased by anthropogenic desertification. In industrialized areas such as much of Europe, North America, Japan, and large cities in Asia, particles are mainly generated by gasoline, diesel, and coal combustion and from condensed organic and metal vapors (WHO, 2003). Particles from urban and industrial areas tend to contain sulfate, nitrate, ammonium, and organic carbon, with smaller amounts of metals and crustal materials. As previously discussed, sulfate (SO_4) is formed when sulfur dioxide (SO_2, often emitted from coal-fired power plants and large industries) either reacts through an aqueous path with hydrogen peroxide (H_2O_2) or is oxidized in the atmosphere by the HO• to form sulphuric acid (H_2SO_4), which has a low vapor pressure. Ammonia (NH_3) reacts with H_2SO_4 to form ammonium sulfate. Nitrate aerosol is formed from gaseous nitric acid (HNO_3) reacting with gaseous NH3 to form condensed phase ammonium nitrate (NH_4NO_3) or reacts with existing alkaline aerosol. Nitric acid is formed whenNO2 is oxidized by the HO• (as discussed above and in Figure 5.4). Ammonia is emitted from livestock manure and other agriculturally related processes, such as spreading natural and synthetic fertilizers, and from vehicle exhaust. Organic carbon particulate can be primary or formed by the condensation of organic gases. There are many sources of organic gases (discussed above). In less developed areas, such as parts of Africa and Asia, biomass burning is the principal source of regional aerosol pollution, resulting largely in elemental and organic carbon particles and nitrate. Dust storms largely contribute mineral particles.

Many measurement and modeling studies, as well as satellite measurements, have now shown that aerosols can cover large geographic areas. Dust storms from as far as the Sahara and Gobi deserts have been observed to impact western Europe (Gerasopoulos *et al.*, 2003; Aymoz *et al.*, 2004), various sites across the United States (Perry *et al.*, 1997; Prospero, 1999; Liu *et al.*, 2003; DeBell *et al.*, 2004; Kim and Hopke, 2004), and western Canada (Jaffe *et al.*, 1999; Husar *et al.*, 2001; VanCuren and Cahill, 2002). Observations in Europe have even recorded the effects of Asian dust that traveled across the Pacific,

North America, and then the Atlantic (Grousset *et al.*, 2003). Episodes of dust can be striking because dust during these storms can far exceed anthropogenic emissions (Penner *et al.*, 2001). At least one modeling study suggests that transported Asian dust also carries with it significant anthropogenic particulate matter (Takemura *et al.*, 2002), suggesting, for example, that Asian anthropogenic emissions could have a significant influence on particulate matter concentrations in western North America.

Biomass burning also creates potent pollution events. Large forest fires in Canada were observed to impact air quality in the United States (Wotama and Trainer, 2000), including a smoke plume from wildfires in Quebec, Canada, measured as far south as Virginia (DeBell *et al.*, 2004). Fires in Mexico and Guatemala were also found to impact air quality in the United States (Rogers and Bowman, 2001; Tanner *et al.*, 2001), and smoke from Central American and southern Mexican forest fires was captured in satellite images traveling across the United States and into Canada (Figure 5.6). During this air pollution event, visibility in many Texas cities was less than one mile (EPA, 2003b). Satellite images can track and quantify important properties of biomass burning and dust storm events (Falke *et al.*, 2001; Husar *et al.*, 2001; Hillger and Ellrod, 2003), and information from these images can be verified and enhanced by comparison with ground-based measurements, which provide more detail in chemical composition and in aging and mixing effects (DeBell *et al.*, 2004).

Other studies have demonstrated the regional extent of $PM_{2.5}$ and PM_{10} from urban sources, such as across state boundaries in the United States (Chameides and Cowling, 1995b; Baumgardner *et al.*, 1999; Sister and Malm, 2000; Ames and Malm, 2001; Odman, 2002a; Bergin *et al.*, 2006c), across North American nations such as the United States and Canada (68, 80), and between the nations of Europe (Querol *et al.*, 2004). A recent modeling study calculated the sensitivity of $PM_{2.5}$ concentrations in 19 eastern U.S. states to SO_2 emissions from other states and found that on average 75% of

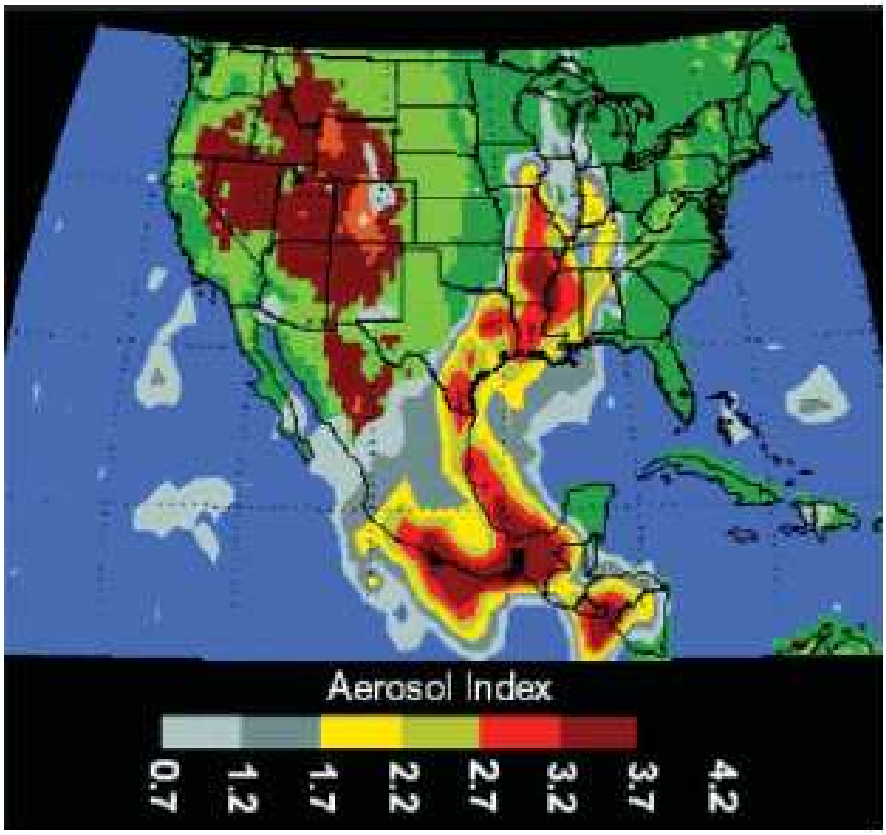


Figure 5.6. Satellite image from the Earth Probe Total Ozone Mapping Spectrometer of smoke/dust (absorbing aerosols) over North America on May 15, 1998 (EPA, 2003b). Image developed by the Earth Observatory team, GSFC/916, and reproduced with permission.

$PM_{2.5}$ in most of these states was sensitive to reductions in regional SO_2 emissions (Figure 5.7) (Bergin *et al.*, 2006c). Another U.S. study used back trajectories and fine sulfate measurements and found roughly half of the sulfate in New York state originated from regional sources (Dutkiewicz *et al.*, 2004). A global modeling study (Park *et al.*, 2004) found that transboundary transport of particulate matter and its precursors dominated natural sources in the United States and that up to 30% of the transboundary particulate matter was due to transport from Asia. Each of these studies highlights the need to address regional transport in developing efficient aerosol pollution reduction plans.

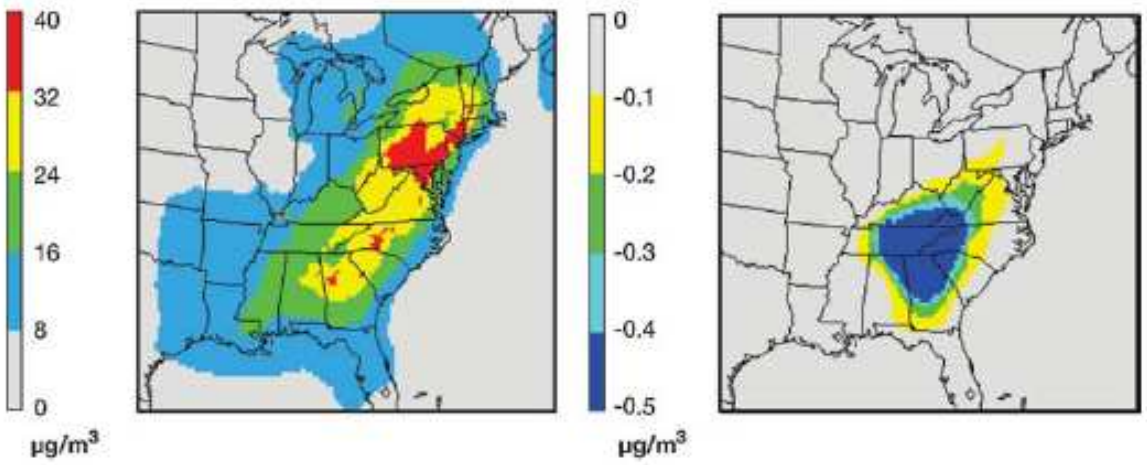


Figure 5.7. Regional particulate matter and its sensitivity to emissions. (a) Simulated 24-hour averaged $PM_{2.5}$ concentration and (b) its sensitivity to a 30% reduction in SO_2 emissions from Tennessee (Bergin *et al.*, 2006b).

5.3.4 Mercury

Although other toxic metals (e.g., lead) are known to be transported long distances and introduced to the environment through atmospheric pollution, mercury (Hg) is proving to be the most serious of these metals. Mercury, particularly in the form of methylmercury (CH_3Hg) or (MeHg), is highly toxic to humans and other animals, and evidence has shown that mercury threatens the health of humans and wildlife even in areas that are not obviously polluted (USGS, 2000). Concentrations are highest near emission sources, but gaseous elemental mercury can circulate on a global scale, and anthropogenic emissions have resulted in worldwide chronic, low-level environmental exposures (NRC, 2000). Even at very low atmospheric deposition rates in remote locations, the bioaccumulation of mercury can result in toxic effects (USGS, 2000). Although mercury is dispersed globally, differences in sources, emission densities, deposition patterns, aquatic and terrestrial environments, and exposure related behaviors lead to varying impacts in different regions.

Mercury affects the immune system, alters genetic and enzyme systems, and damages the nervous system (USGS, 2000). Developing embryos are five to ten times more sensitive to damage by MeHg, which rapidly crosses the placenta, than are adults (USGS, 2000), and young children are especially susceptible to mercury's neurotoxic effects (86). For these reasons, pregnant and nursing woman and young children are the most sensitive human populations to poisoning (87). Humans are exposed to MeHg almost entirely by eating contaminated fish and animals that are at the top of aquatic food chains (USGS, 2000). In the United States, 45 states issued mercury advisories in 2003 for limiting the consumption of certain fish from freshwater lakes and rivers, coastal waters, and marine environments (87). Even with these advisories, it is estimated that over 60,000 children are born in the United States each year at risk for adverse neurodevelopmental effects caused by in utero exposure to MeHg (NRC, 2000). Although difficult to prove, studies clearly indicate that ingesting contaminated fish also poisons many aquatic birds and other wildlife (USGS, 2000). Predators such as large fish and aquatic birds can have mercury levels more than a million times higher than those in the surrounding environment (Little, 2002).

Some mercury occurs naturally in the environment; however, atmospheric deposition is the dominant source of mercury over most of the landscape (USGS, 2000). Once in the atmosphere, mercury can disperse widely and circulate for years after emission through a series of "hops" via atmospheric transport, deposition, and evaporation back to the atmosphere (USGS, 2000; UNEP, 2003; EC, 2004) (Figure 5.8). Sedimentation or entry to the food chain will eventually remove it from this cycle.

Most mercury is emitted as nonreactive, inorganic mercury vapor, Hg^0, although a substantial fraction is in the form of reactive gaseous mercury, Hg^{2+}. In the atmosphere, Hg^0 is oxidized to form HgO (or Hg^{2+}) by both gas phase and aqueous reactions

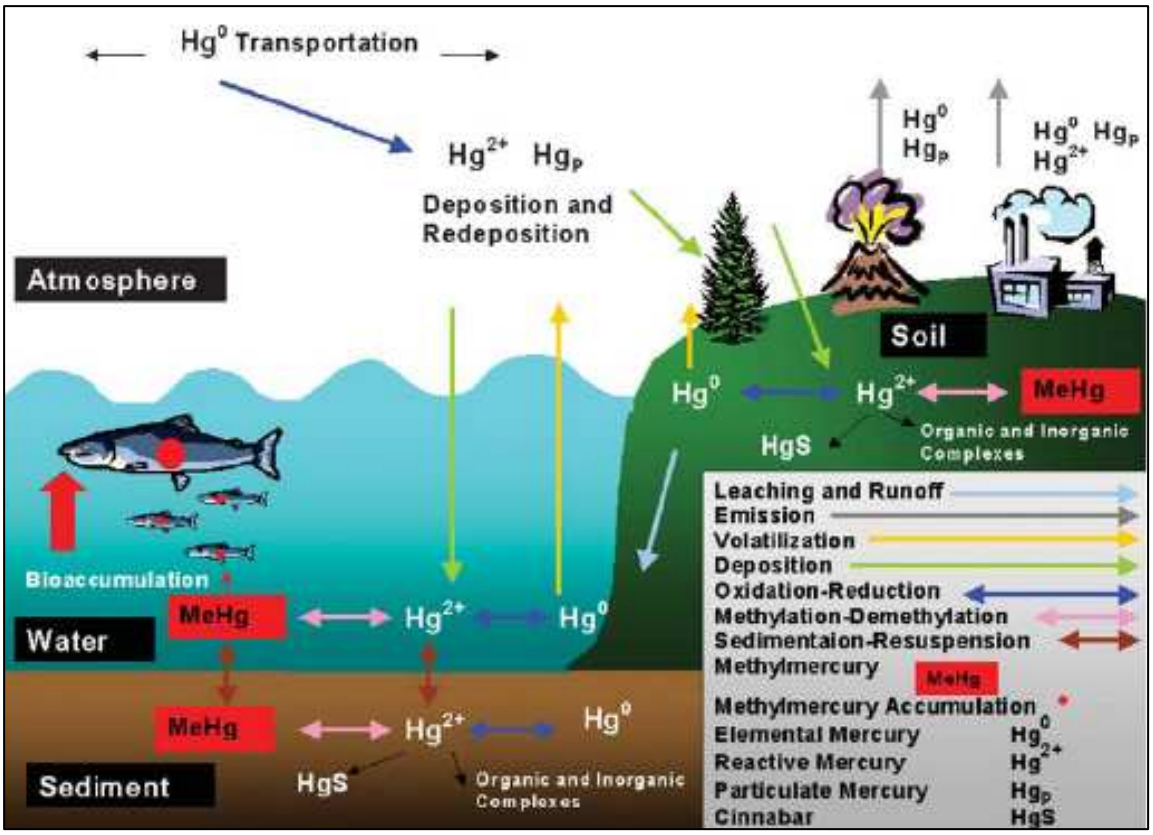


Figure 5.8. Conceptual biogeochemical mercury cycle. Reproduced with permission from (EnvCan, 2004).

(Shia *et al.*, 1999; Sommar *et al.*, 2001; Ryaboshapko *et al.*, 2002; Seigneur *et al.*, 2003; Pal and Ariya, 2004). Hg^{2+} rapidly deposits out of the atmosphere. HgO has a relatively low vapor pressure, so it may exist in the gas phase or may condense on preexisting particulate matter. This form is soluble in water and can be absorbed in cloud droplets or rain, where it can react to form $Hg(OH)_2$ and $Hg(Cl)_2$; the latter is preferred if much HCl is present. Transfer to land and water occurs both by wet and dry deposition, with wet deposition dominating (Seigneur *et al.*, 2004). The lifetime of Hg^0 in the atmosphere is generally estimated to be approximately 1.2–1.5 years (Seigneur *et al.*, 2004), although new findings strongly indicate a much smaller lifetime of about 1 or 2 months (Renner, 2004). Some studies suggest that this more rapid oxidation may be due to reactions with halides (at the poles and temperate marine boundary layer) and urban pollutants, most

likely ozone (Renner, 2004). This shorter lifetime suggests that deposition occurs much more rapidly than previously estimated and therefore current emissions are likely higher than estimated. One such underreported source may be gold mining activities, as discussed below. Typical background concentrations of Hg^0 are about 1.2–1.6 ng/m^3. Hg^{2+} is found in the pg/m^3 range, showing greater spatial variability than Hg^0 because it is more reactive.

The most toxic form of mercury, CH_3Hg, bioaccumulates through the aquatic food chain. Mercury reaches aquatic systems through deposition, runoff, or direct discharge (e.g., during gold mining). Transformation of inorganic mercury vapor to MeHg proceeds either indirectly via atmospheric reactions, with subsequent transformation in terrestrial organisms, or directly by bacteria in aquatic systems that normally process sulfate. The bacteria containing MeHg can then be consumed or may excrete the MeHg to the water, where it can adsorb to plankton, which can then also be consumed (USGS, 2000). Certain types of wetlands (e.g., coastal), dilute low-pH lakes and newly flooded reservoirs, and coastal wetlands are known to favor the production of MeHg (USGS, 2000). Once the mercury has entered the food chain through bacteria, it bioaccumulates in higher animals.

There is a great deal of variation in estimates of the mercury contributions to the atmosphere from anthropogenic, natural, and reemitted mercury sources, which may have originated from natural or anthropogenic sources (ATSDR, 1999). The U.S. Environmental Protection Agency (EPA) currently estimates that natural sources contribute about a third of current global mercury air emissions, and anthropogenic emissions make up the remaining two thirds (EPA, 2004c). Between 2143 and 1049 Mg [Mega grams (10^6)] of new anthropogenic and biogenic emissions are estimated to be released per year (Seigneur *et al.*, 2004), respectively, and another 3201 Mg/yr are reemitted emissions. Of this, 2134 Mg/yr are likely reemitted anthropogenic mercury, in essence doubling the effective rate of emission. About three quarters of the total

anthropogenic emissions of mercury in 1995 are attributed to combustion of fossil fuels (Pacyna *et al.*, 2003), particularly in coal-fired power plants (NRC, 2000; EPA, 2004c). It was estimated that Asian countries contribute over 50% of the total emissions (Pacyna *et al.*, 2003), chiefly from coal combustion in China, India, and South and North Korea (Munthe and Palm, 2003) (Figure 5.9). Though firm numbers are not yet established, recent estimates indicate that artisanal gold mining activities release between 800 and 1000 Mg per year into the air, water, and soil combined (Hinton and Veiga, 2004), which is much larger than previous estimates (e.g., 300 Mg/year) (UNEP, 2003). These releases generally result in heavy local deposition (Hinton and Veiga, 2004), and this source category will have more significant regional (and global) impacts than previously estimated. This potentially large adjustment to estimates of emissions highlights the underlying uncertainties in source attribution and the difficulties of identifying the best controls for this pollutant.

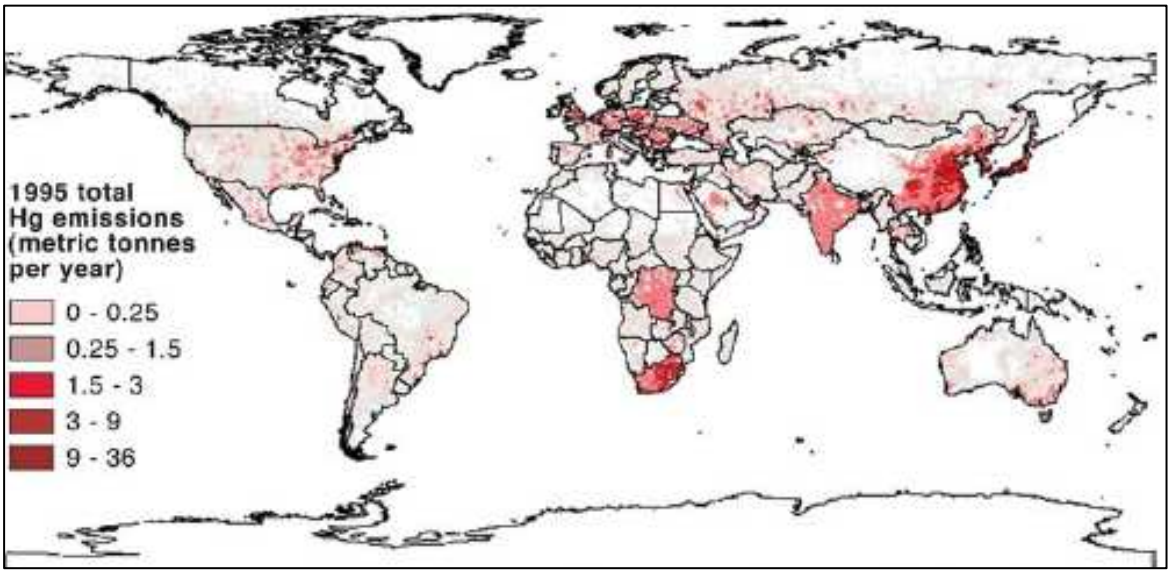


Figure 5.9. Estimated global emissions of mercury in 1995. Reproduced with permission from (Pacyna *et al.*, 2003).

The potential for regional and long-range transport of mercury emissions is dependent on the chemical form in which the mercury is emitted and how fast it is transformed. As we gather more observations of the speciation of anthropogenic emissions and their oxidation (and reduction) rates, our understanding of the relative importance of global, regional, and local sources is evolving. In 1997, the U.S. EPA estimated that anthropogenic emissions in the United States were responsible for 60% of deposition in the 48 contiguous United States, and 40% of deposition was from natural sources, human activities outside the United States, and U.S. emissions returning via global cycling. Approximately two thirds of U.S emissions are transported outside the United States (EPA, 1997b). Other studies have suggested that anthropogenic U.S. emissions contribute less than 20% of the deposition observed throughout most of the United States, with maximum local contributions of up to 80% in a few locations (Seigneur *et al.*, 2004). Similar estimates have been made for European countries (EMEP, 2004b).

5.3.5 Persistent Organic Pollutants

Persistent organic pollutants (POPs) are toxic organic substances that widely disperse, persist in the environment, bioaccumulate through the food web, and pose a risk to human health and the environment (Hooper and McDonald, 2000; UNEP, 2004). Concentrations can magnify in fatty tissues by up to 70,000 times background levels (WorldBank, 2004). POPs enter humans chiefly through animal-derived food (fish, poultry, beef, eggs, and dairy products) and have been linked to causing, among other effects, cancer, damage to the nervous system, reproductive disorders, behavioral disorders, and disruption of the immune and endocrine systems (Solomon and Mahalingaiah, 2001). Because of their fat-seeking properties, POPs magnify in infants through both in utero transmission and breast-feeding. Human breast milk concentrations of some monitored POPs have been increasing exponentially, and these concentrations

serve as one indicator of past human exposures and environmental conditions as well as conduits that magnify concentrations in the next generation (Hooper, 1999). Previously unrecognized POPs (i.e., brominated biphenyl ethers) have been identified owing to increasing concentrations found by systematic monitoring of chemicals in human breast milk in Sweden after they banned the use of seven other POPs in the 1970s (Solomon and Mahalingaiah, 2001).

The most commonly recognized POPs are partially oxidized and/or halogenated organics, often including one or more aromatic structures. Although there are hundreds of POPs currently in the environment, 12 have gained particular interest and have been tagged as "the dirty dozen": DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, toxaphene, hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), dioxins, and furans. These compounds have been used as pesticides (e.g., DDT, aldrin, dieldrin, endrin) in past consumer or industrial applications, such as coolants, flame retardants, lubricants, and sealants (e.g., PCBs), or are generated unintentionally as by-products of various combustion processes, such as medical waste incineration (e.g., polycyclic aromatic hydrocarbons (PAHs), dioxins, and furans).

Common characteristics of POPs are their semivolatility and/or partial water solubility. These characteristics lead to their ability to be transported in the atmosphere both in the gaseous and condensed phases (associated with particulate matter), deposited, and then reemitted through a repeated (and often seasonal) cycle of evaporation and deposition (similar to mercury, as described above.) With lifetimes from a few years to decades long, which are increased by halogenation, POPs released in one part of the world may circulate regionally and globally (Munthe and Palm, 2003) via the atmosphere, oceans, and other pathways, traveling far from their original point of emission(EPA, 2004d).

Atmospheric monitoring data for POPs are sparse, and global emission distributions are poorly characterized. Much of what has been learned about POP

transport and impacts in the United States has come from the study of contamination of the Great Lakes region, which, for many years, was a receptor of industrial and agricultural pollution from within the Great Lakes' watershed and beyond. All 12 of the dirty dozen POPs have been identified in Great Lakes' fish and wildlife, even though some of these compounds were never used in significant quantities in the region. As a result of the contamination, consumers of the regions' fish have up to eight times the body burden of POPs as the general public. The regional transport and deposition of POPs (and heavy metals) in Europe have been demonstrated through modeling (e.g., Figure 5.10) (EMEP, 2004a). Further evidence of long-range transport comes primarily from the detection of POPs in remote locations, such as remote marine or polar environments where there are no emission sources. POPs are transported to the poles via episodic transport from industrialized source regions or through the cycle of deposition and reemission described above, which acts as a global distillation process. Once in the colder environments at the poles, semivolatile POPs condense and accumulate (Rodan, 2002).

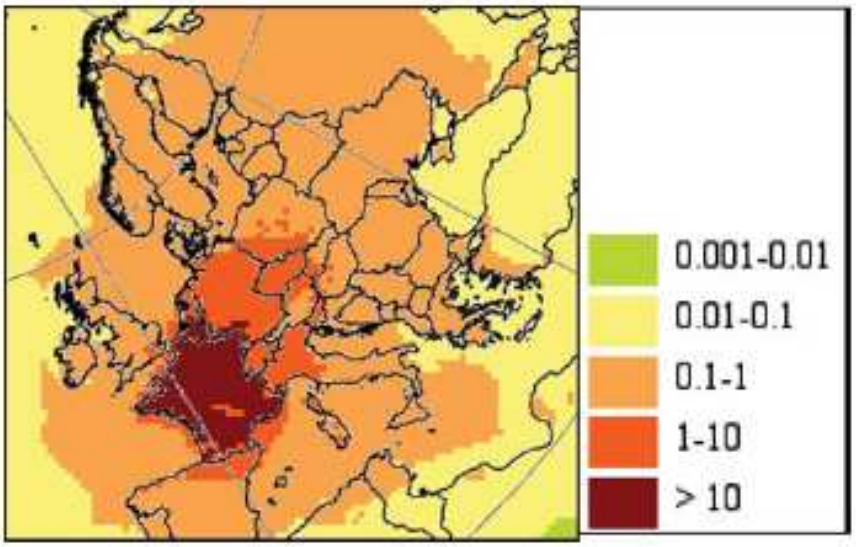


Figure 5.10. Modeled benzo[a]pyrene (BaP, a PAH) depositions from emissions in France in 2001, g/km2/year. Reproduced with permission from (EMEP, 2004a).

Recognizing the need for addressing the POP problem across boundaries, the dirty dozen are targeted to be banned or restricted by the Stockholm Convention on POPs, which was signed in May 2001 by over 100 countries (UNEP, 2001), although DDT will continue to be used in some countries that have high malaria risks until a suitable alternative is developed. Additionally, new regulations under consideration in the European Union (E.U.) [REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals, (EurComm, 2004)] would restrict the use of other POPs in chemicals manufactured in or imported to E.U. nations. This program is discussed below.

5.3.6 Regional Climate Change

Concern over global climate change derives from observed increases in the atmospheric concentrations of long-lived greenhouse gases, which are known to absorb heat in the form of infrared radiation, as well as from observed increases in global mean temperature (IPCC, 2001). However, although there is substantial evidence for concern about climate change, projecting future climate remains highly uncertain owing to uncertainties in emissions, the influence of pollutants, and feedback processes, which may enhance or counteract warming. Even though anthropogenic aerosols and tropospheric ozone are known to influence the climate system, some of the uncertainties associated with their influence are among the most important in our current understanding (IPCC, 2001).

Particulate matter has multifaceted impacts on climate. Most fine particles, such as sulfate, scatter light very efficiently, causing solar radiation to be redirected away from the Earth, resulting in a cooling effect on ambient temperature. Black carbon particles (soot) absorb light and therefore may have a warming effect (Chameides and Bergin, 2002). However, because these aerosols have different spatial distributions (and different distributions than greenhouse gasses), their effects do not simply offset each other. Particles also serve as cloud nuclei, increasing the number of cloud droplets but

decreasing the average cloud droplet size. This causes an increase in cloud albedo (cooling) and less precipitation (Chameides *et al.*, 2002), which can have manifold effects. Aerosol effects on temperature include altering regional atmospheric stability and vertical motions, impacting both large-scale circulation and the hydrologic cycle, all with significant regional climate effects (Menon, 2002). The situation is complicated by the fact that the impact of aerosols depends on ambient chemical and physical properties of the particles that are not yet well characterized.

Ozone also has a complex relationship with climate. Tropospheric ozone ranks only behind carbon dioxide and methane in anthropogenic contributions to the global average radiative forcing and is expected to increase the global average temperature over the next decades (IPCC, 2001). As climate changes, the resulting changes in regional climate are expected to increase urban ozone concentrations in many areas, particularly during highly polluted episodes (Hogrefe *et al.*, 2004).

Natural climate patterns clearly impact air pollution formation and transport (as discussed above), and evidence strongly indicates that air pollution also impacts climate. Political bodies must address questions such as whether to act under the current understandings and uncertainties, and if so, how to coordinate or prioritize mitigation efforts and who is responsible for reducing emissions. Although much attention has focused on the global scales of climate change, regional-scale impacts have also been identified and may become more important in the future.

5.3.7 A Unified View

Each pollutant has distinct regional characteristics, yet they are intimately linked by the chemistry and physics of the atmosphere, as well as by common sources and possible controls. Their linked chemistry and common sources present strong arguments for addressing them simultaneously to identify the most effective control policies. For

one example, consider relationships between acids, ozone, mercury, and particulate matter—four important regional pollutants (Figure 5.4).

First, they have common sources. Sulfuric and nitric acids are due, respectively, to the oxidation of sulfur dioxide and nitrogen oxides. These precursors are also responsible for a large fraction of aerosol pollution, and NO_x is a main precursor of tropospheric ozone. The major anthropogenic source of sulfur dioxide is electricity generation, primarily from coal-fired utility boilers, which also emit mercury. Power plants are also a major source of NO_x, along with mobile sources and fires, both of which also emit organic and elemental carbon particles and VOCs.

Second, NO_x (as NO_2) and SO_2 are oxidized in large part by the hydroxyl radical, HO•, which also initiates the VOC reactions that drive much pollution, such as ozone and aerosol formation. Ambient HO• levels are particularly important in affecting the O_3 formation rate in the presence of NO_x because reaction with HO• is a major (and in many cases the only) process that causes most VOCs to react. The HO• is also instrumental in the transformation of other air pollutants, such as oxidizing Hg0 to Hg^{2+} and initiating atmospheric destruction on POPs. Further, most of the HO• comes from ozone photolysis.

Third, particulate matter and ozone both impact climate (as discussed above). Obviously, these regional pollutant systems—acids, ozone, and particulates—and, to a lesser extent, mercury and POPs are tightly linked chemically and are, indeed, virtually inseparable.

5.4 Management of Regional Transboundary Air Pollution

Whereas meteorological and emission patterns, and other physical causes create different spatial distributions of pollutants, management of air quality is bounded by politics, economics, and cultures. Regional pollution can cross state, provincial, national, and even continental boundaries, and each of these entities can have very different air

quality goals and management strategies. Air pollution often has a relatively clear upwind-downwind dimension, in which emissions from a source nation (or state) affect air quality in a receptor nation (or state) much more strongly than vice versa. Part of the downwind nation's pollution problem, therefore, may be beyond its jurisdiction to control. This situation is conceptually similar to the case of a single polluting industry affecting a population, which may be resolved through government regulation. On an international level, however, a higher government authority is often lacking. A fundamental issue in regional transboundary air quality control, whether across state or national boundaries, is how to encourage or coerce upwind jurisdictions to reduce emissions, even when they do not perceive it to be in their self-interest.

Most national governments regulate ambient air pollution through the creation and enforcement of air quality standards. In some nations, such as the United States, an agency of the federal government sets standards and determines and enforces compliance, and state or provincial governments are responsible for implementing actions to meet those standards. The goal for state and local air quality managers, then, is to achieve compliance with standards for several pollutants at low cost (both economically and politically). Air quality goals are balanced against other considerations, including transportation and energy needs and business and consumer interests.

Regional air pollution raises problems for such a state-focused system. Upwind states may have their own motivations for reducing emissions, or they may not. A state may be influenced so strongly by emissions from other states that even the complete elimination of in-state emissions may not be sufficient to achieve standards, especially for secondary pollutants such as ozone and some $PM_{2.5}$. Such upwind-downwind disparities can be reinforced by differences in geography, economic well-being, vested economic interests, and even culture and philosophy. Not surprisingly, densely settled, affluent downwind jurisdictions in violation of standards often emphasize their rights to breathe clean air and not be affected by upwind emissions. Jurisdictions that are upwind,

protective of industry, and have smaller, more dispersed populations tend to emphasize their rights to emit (Farrell, 2001). Downwind areas may have already exhausted the most cost-effective controls, while many options may remain untapped upwind. An overall most cost effective strategy might then include upwind controls(Shih *et al.*, 2003). As will be discussed below, similar issues arise for international communities, although cooperation is much more difficult to attain between areas without a unifying government structure.

A political jurisdiction that is impacted by transboundary air pollution can attempt to address the sources of pollution either by taking unilateral actions, by forming a cooperative regime, or (if available) by appealing to a higher governmental authority. Unilateral action may take the form of research and education programs designed to change awareness, perceptions, and behaviors in the upwind jurisdiction. Alternatively, a downwind jurisdiction may use the leverage of trade regulations to affect source behavior in upwind jurisdictions. For example, the European Commission's proposed chemical legislation REACH may help reduce global sources of certain POPs by restricting access to a large portion of the global market, forcing manufacturers to develop alternatives. In most cases, however, decreasing upwind emissions will require the development of some type of cooperative regime (Ostrom, 1990). Here, we use the term regime to mean "social institutions consisting of agreed-upon principles, norms, rules, procedures, and programs that govern the interactions of actors in specific issue areas" (Young, 1999). That is, a regime encompasses a whole process of interaction, including both scientific and political activities, with or without formal agreements. Examples of such cooperative regimes range from technology transfer and research efforts to the establishment of formal emission reduction obligations or emission trading markets.

In the next section, we present three examples of management programs or cooperative regimes from the United States and Europe where this collective action problem has been (at least partially) successfully addressed. We then more generally

consider the conditions under which regimes for transboundary air pollution are most likely to succeed and assess the capabilities and potentials of existing regimes for addressing regional air pollution around the world.

5.4.1 Examples of Transboundary Air Quality Management Regimes and Approaches

5.4.1.1 Emission Trading of SO_2 for Acid Deposition Control

Arguably one of the most effective regional air pollution control programs to date was also one of the more controversial at the time of inception. Trading of SO_2 emissions was introduced as part of the 1990 U.S. Clean Air Act Amendments (CAAA) to deal with the major precursor of acid deposition (as well as of sulfate aerosol) and is a core component of the Acid Rain program. As opposed to the more historic "command and control" approach by which the government specified the type of controls to be used by individual plants, a market was designed with a fixed number of emission allowances that could be bought, sold, or traded. Companies that could reduce emissions inexpensively could reduce their emissions to less than their initial allocation and sell the extra allowances. Industries that had higher control costs could buy these extra allowances, reducing their control needs.

As designed, and as realized in practice, the market seeks the lowest cost approach to achieving the desired emission reductions. The program was designed to cut SO_2 emissions from power plants to half of 1980 levels by 2010. By 2003, the program had achieved a 38% reduction from 1980 levels (EPA, 2004b). Initial estimates suggested that the cost of the reductions would be between $4 and $8 billion per year; however, recent estimates suggest that the costs of the program have been about $1 billion per year (http://www.etei.org/handbook/chapter 2/09.html). The reductions achieved through the Acid Rain program will be expanded through the implementation of the recent Clean Air

Interstate Rule, designed to achieve an additional 67% reduction over 2003 levels (http://www.epa.gov/cair/). The success of this program has spawned similar approaches to dealing with NO_x and VOC emissions for ozone control. An emission trading program in Los Angeles uses trading zones (upwind and downwind) to assure that trading tends to decrease emissions where reductions are most beneficial (http://www.aqmd.gov/reclaim/).

5.4.1.2 Regional NO_x Control for Ozone in the United States

Regional control of NO_x to reduce ozone in the eastern United States is an example of both success and failure. By the early 1990s, the scientific community generally understood that ozone could move between states and that controlling emission of NO_x was most important for addressing transported ozone (NRC, 1991). However, this understanding was not necessarily shared or considered credible by all federal and state government actors (Farrell and Keating, 2002). The Ozone Transport Commission (OTC) was formed in the 1990 CAAA to consist of 12 east coast states (Maine to Virginia) and ultimately achieved success in cooperatively reducing interstate NO_x emissions. Because the ozone nonattainment region stretched continuously across many of these (mostly small) states, and most states were both upwind and downwind of nonattainment areas, the need for cooperative action was apparent. The OTC states, with technical support from the EPA, agreed to cap their collective emissions of NO_x from large electric power plants and to achieve the emission reductions through an internal emission trading program. Reaching this agreement required overcoming concerns about the effect of a trading system on the locations of emissions and the consequent effects on both ozone concentrations and on the economies of the different states. The OTC succeeded because it created a framework by which states were mutually assured that all states would be subject to similar controls and that the overall costs of emission reductions would be reduced through trading. Achieving this agreement took almost a decade and required the

formal structure and frequent technical and political meetings that the OTC provided, which generated trust among the participating states (Farrell, 2001).

As the OTC efforts were taking shape, additional analysis revealed that emissions from states upwind of the OTC states had important effects on ozone in OTC nonattainment areas. In 1995, the Ozone Transport Assessment Group (OTAG), comprised primarily of representatives of the EPA and the 37 states in the eastern half of the United States, was created to conduct the largest assessment at the time of transboundary ozone. The main objective of OTAG was to create an opportunity for the states to cooperatively develop a strategy for addressing regional ozone transport, which was considered preferable to the alternative of direct EPA mandates. Ultimately, the differences between upwind and downwind states and the lack of political leverage to encourage upwind states to reduce emissions were not overcome, and OTAG was able only to reach a weak consensus, recommending a wide range of emission reductions (0% to 80% control) to address the problem. Soon after OTAG ended in 1997, the U.S. EPA exerted its authority to control interstate air pollution transport by requiring 22 states to reduce NO_x emissions, primarily from electric power plants. Only through the authority of a higher governmental body could a regional strategy encompassing more than the OTC states be implemented (Farrell, 2001; Farrell and Keating, 2002). Recently, the U.S. EPA extended its regional NO_x controls in the eastern United States through the Clean Air Interstate Rule (http://www.epa.gov/cair/).

5.4.1.3 Cooperative Air Pollution Control in Europe

The 1979 Long-Range Transboundary Air Pollution (LRTAP) Convention is one of the most successful international regimes addressing environmental problems. Arising out of concern about acid deposition in Europe and initially shaped by Cold War politics, its signatories include all of the nations of Europe (including the former Soviet Bloc), the United States, and Canada. Eight protocols have been successfully negotiated under the

Convention, including agreements to support scientific cooperation and obligations to reduce emissions related to acidification, tropospheric ozone, POPs, heavy metals, and eutrophication. Recently, LRTAP expanded to include several of the former Soviet republics in Central Asia.

The success of LRTAP can be attributed, at least partially, to several factors. First, LRTAP constructed a large technical and analytical support structure, including the Cooperative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollution in Europe (EMEP). This cooperation helped create a shared understanding of the sources and effects of transboundary air pollution, which has been critical to reaching agreements on emission reductions (Levy, 1994). Second, leadership by individual nations has been important in creating pressure for other nations to follow (Levy, 1994). More recently, the expansion of the European Union to include more nations in Eastern Europe has added to the atmosphere of cooperation, as countries that wish to become part of the European Union have sought opportunities to cooperate with the current E.U. members (VanDeveer, 2005). LRTAP's success has taken significant effort and time to achieve. The first several protocols negotiated under LRTAP mainly identified problems, established cooperation, and set easily attainable goals. It was not until the protocols developed in the 1990s that more ambitious obligations for emission reductions were agreed upon (Keating *et al.*, 2004).

5.5 Achieving Successful Regimes for Transboundary Air Pollution

As the previous examples illustrate, forming cooperative international or interstate regimes that include obligations to reduce emissions is an intensive, lengthy process. This lengthy process is unavoidable because the amount of human resources or money is not the deciding factor in reaching an agreement, but "generation of the coordination, cooperation, and trust" is needed to create effective management (Clark and Dickson, 2001).

Although cooperative international or interstate regimes do not always follow set patterns, their evolution can often be described in two phases. The first phase frames the problem—defining the issues, relevant knowledge, and general relationships between the parties responsible for and affected by the problem. Cooperative scientific research plays a leading role during this phase by providing a common understanding of the problem's physical aspects and by creating a cooperative atmosphere. Given that environmental problems are often complex, problem framing also defines the interests and positions of parties, as well as the differences in positions that must be overcome. These differences may be so intractable that no agreement will result, or the regime may agree to accommodate different perspectives while maintaining communications. Consequently, agreements reached within this first phase are typically general, such as setting terms for further cooperation or codifying positions or laws that parties already hold or are likely to adopt (Keating *et al.*, 2004).

The second phase builds on the institutions created in the first phase, allowing for the creation of increasingly complex and substantive policy agreements, which may include emission reduction obligations. During this phase, emphasis is placed less on international dimensions of the problem and more on analysis of collectively beneficial, efficient alternatives. By participating in this lengthy process of technical analysis and negotiation, parties may change their perceived self-interests, with consequent changes in internal policies and negotiating positions (Keating *et al.*, 2004).

Experience with past regimes for transboundary environmental problems illuminates several characteristics of successful regimes. As mentioned earlier, cooperation among technical experts helps foster a shared framing of the problem and builds trust. Effective regimes often develop scientific cooperation before political negotiations and build the technical capacity that supports timely analyses. Such analyses often emphasize consideration of control scenarios and are most effective when considered to be credible (competent and appropriate for decision needs), legitimate (the

assessment process is transparent and impartial), and salient (relevant and timely for decision-making needs) (Clark and Dickson, 2001).

Regimes with fewer parties and with parties that are economically, culturally, or geographically similar tend to be more successful than large heterogeneous regimes. Over time, however, regimes are unlikely to succeed unless they involve all major parties contributing to a problem. Parties that share borders or a regional identity often have other reasons for cooperation, unrelated to the environmental issue at hand. Because the generation of trust is critical for a successful regime, parties that have a history of cooperating on other issues may be more likely to succeed. Initially, regimes require the leadership of a sponsor, often a party affected by upwind emissions who will invest the resources to establish and maintain institutions. These sponsors have lasting influence on how problems are framed.

Alternatively, large cultural and economic differences can make communication difficult and hinder success. International pollution transport involving both industrial and developing nations may expose differences in social priorities, capabilities to support emission reductions, technical capacity, and government regulatory abilities. Participating in regimes may stretch the limited technical resources often found in developing nations, exposing an unfair balance in the negotiation process. The most important short-term action in working with developing nations is to provide support for the technical and management capabilities of these nations on domestic air pollution issues. Doing so will increase the capacities of developing nations to participate meaningfully in international regimes and to address the important air pollution issues existing in their own growing urban areas. In many cases, awareness and motivation to address air pollution already exist, but the lack of technical and government capacity limits prospects for emission reductions. Supporting these capacities would allow developing nations to address their worst air pollution problems, with consequent benefits

such as reduced long-range air pollution transport (Keating *et al.*, 2004) and reduced greenhouse gas emissions (West *et al.*, 2004).

Because trust is so important, successful regimes develop both interpersonal trust between key actors and institutional trust. Institutional trust can be developed through leadership that is perceived as impartial, that promotes decision making in a process perceived as fair, and that allows for the participation of all relevant parties. Ensuring the accountability of parties in fulfilling commitments, such as through reporting systems and implementation review bodies, is also vital for maintaining trust. Management and coordination are also important, and institutions with strong central secretariats or administrators are more likely to succeed, as are financially strong and technically capable regimes. Institutions should also be able to adapt to changes in understanding or environmental or political conditions. When natural or political events or scientific discoveries focus public and political attention on an issue, effective regimes are capable of acting quickly to take advantage of such windows of opportunity (Keating *et al.*, 2004).

5.6 Assessment of Existing International Regional Regimes

Although regional transboundary air pollution is also relevant within nations, this section addresses the major international regimes addressing regional transboundary air pollution. We first consider the current status and prospects for future growth of existing regimes in Europe, North America, and Asia and then explain how regimes can address problems of related transboundary air pollution beyond regional scales.

5.6.1 Europe

For twenty years, LRTAP has been the dominant forum for addressing transboundary air pollution in Europe. Since 1999, however, policies set by the European Commission have driven cooperation in Europe. As the European Union continues to

expand (http://europa.eu.int/pol/enlarg/overview en.htm), more LRTAP parties will be subject to policies formed in Brussels. In the meantime, LRTAP will continue to become less relevant as a policy-making institution for the European region.

Given this political reality and the growing scientific evidence that many of the pollutants addressed by LRTAP are affected by flows beyond the current geographic scope of the Convention, the LRTAP Executive Body acted in December 2004 to form a new EMEP task force to examine the evidence for hemispheric transport of air pollution (www.htap.org). This task force, to be chaired by the United States and the European Commission, will seek to build the scientific foundation for considering future policy initiatives that would involve additional countries outside the current geographic scope of the Convention.

5.6.2 North America

The United States and Canada have a long history of cooperation addressing transboundary air pollution, which began in the 1980s with concerns over acid rain and led to the 1991 Canada-United States Air Quality Agreement and 2000 Ozone Annex. Similarly, the United States and Mexico have worked to address issues of air pollution mainly along the border (focusing less on regional transboundary pollutant flows) through the 1983 La Paz Agreement and the Border 2012 program, which includes agreements and mechanisms to work toward broad environmental goals and includes funding for pilot projects to reduce emissions in targeted areas. The North American Commission on Environmental Cooperation comprises the United States, Canada, and Mexico, and although it has helped coordinate the exchange of information and continent-wide analyses, it has not served as a forum for negotiating emission reductions. NARSTO (formerly the North American Strategy on Tropospheric Ozone) was established in 1995 with the goals of coordinating policy-relevant scientific research and assessment between Mexico, the United States, and Canada and of addressing local and

regional air pollution management (NARSTO, 2000; NARSTO, 2003). NARSTO has coordinated and supported many scientific endeavors, such as NARSTO-NE, EPA Supersites, and SOS.

In North America, emissions in Mexico have little effect on air quality in Canada and vice versa. Bi-national agreements between the United States and both Canada and Mexico will continue to be the focal point of regional air pollution agreements, and we expect these agreements to expand to include more ambitious reductions and more pollutants. Future efforts may also seek cooperation with the nations of Central America and the Caribbean area and may include efforts to build awareness and capacity in these nations on regional air quality issues. The United States has become increasingly concerned over the effects of forest fire emissions from Central America on air quality in the United States.

5.6.3 Asia

Asia is clearly an area of concern regarding the future growth in air pollutant emissions. Technical knowledge and experience in managing air pollution is generally weak but improving in Asia, and cooperative regimes to address regional air pollution issues are in their early stages. Three regimes currently exist in east Asia and south Asia, focusing mainly on supporting rural air quality measurements to provide an understanding of regional air pollution. The Association of Southeast Asian Nations, composed of 10 nations, developed a 1995 Cooperation Plan on Transboundary Pollution. This was followed by a 2002 Agreement on Transboundary Haze Pollution, which was motivated by the prevalence of haze in this region from large and uncontrolled forest fires. Second, EANET, founded in 1998, involves the participation of 12 east Asian nations. Like LRTAP, it mainly focuses on measurements and analysis related to SO_2 emissions and regional acidifying deposition. The United Nations Environment Programme (UNEP) serves a coordinating function, and Japan, which lies downwind of

major Asian industrial centers, provides substantial support. Finally, the Mal´e Declaration on Control and Prevention of Air Pollution and Its Likely Transboundary Effects for South Asia also began in 1998, involving eight nations in South Asia. Again, the focus of the Mal´e Declaration to date has been in capacity building and support of rural air quality measurements.

Although the existence of these three regimes is very encouraging, none of them have yet succeeded in finalizing agreements on emission reductions. Many Asian countries are focused on air pollution problems at the local or urban scale, such as through the World Bank's Clean Air Initiative for Asian Cities, but transboundary air pollution may be considered a low priority. However, these regional regimes both increase the awareness of transboundary air pollution issues and increase general cooperation among these nations. Already, scientific findings from several recent measurement campaigns in Asia, including the Indian Ocean Experiment (Lelieveld *et al.*, 2001), Aerosol Characterization Experiment (ACE)-Asia (Huebert *et al.*, 2003), and China Map (Chameides *et al.*, 1999) have brought a great deal of attention to the "atmospheric brown cloud" and regional air pollution in Asia. Although these studies were enlightening, they were conducted with little participation from Asian nations and resulted in some caution and distrust in Asia about the motivations of western scientists. Additionally, western scientists have found that the differences in the capacity and interests of political and scientific communities in some Asian countries obstruct crosscultural collaborations. As science has recently improved the understanding of regional transport in Asia, there has been somewhat more of an atmosphere of blame than of cooperation regarding emission responsibilities.

5.7 Regimes to Address Pollutant Transport Beyond the Regional Scale

Successful environmental regimes exist for problems that are clearly identified as global, such as the 1992 United Nations Framework Convention on Climate Change

(UNFCCC) with the resulting 1997 Kyoto Protocol and the 1985 Vienna Convention on the Protection of the Ozone Layer with the resulting 1987 Montreal Protocol. None of these agreements, however, addresses the air pollutants discussed in this review (with the exception of methane, which affects tropospheric ozone), even though some have impacts beyond the regional scale. However, two global regimes been recently been established to address POPs and mercury. The 2001 Stockholm Convention on Persistent Organic Pollutants was signed by 151 nations to bring reductions in emissions of 12 POPs, and the Global Mercury Program was initiated by UNEP following the Global Mercury Assessment (UNEP, 2003). The UN FCCC and Kyoto Protocol could serve as future forums to address tropospheric ozone and particulate matter, which affect climate (Rypdal *et al.*, 2005). The Intergovernmental Panel on Climate Change, which produces scientific assessments related to the UNFCCC, has begun to focus on the linkages between traditional air pollutants and climate change.

Institutions are lacking for dealing with the long-range transport of air pollutants, such as ozone and fine particles, at the hemispheric or global scale. This gap may be filled by (a) geographically extending the participation of existing regimes, perhaps by having existing regimes negotiate or combine together, or (b) creating new, larger scale regimes (Holloway *et al.*, 2003). Creating new regimes or expanding existing ones will take time and progress may be quicker if existing relationships or institutions, such as UNEP, World Meteorological Organization (WMO), or World Health Organization (WHO), can be used as a foundation to begin the building of trust.

Control of air pollution beyond the regional scale must address emissions from developing nations. In addition to Asian emissions, emissions from the Middle East, Africa, and Latin America are of concern, and the formation and development of cooperative international regimes in these areas should be encouraged. New regimes have recently been developed in southern Africa (the Air Pollution Information Network

Africa and its Harare Resolution) and in the Middle East (the Bahrain Code of Environmental Conduct for the Middle East).

5.8 Summary and Conclusions

Although there is still much to be learned about the regional nature of different air pollutants, our current scientific understanding recognizes that transboundary air pollution is common and its damage extensive, making political cooperation necessary, and suggests that future management efforts must integrate the linkages between pollutants across large geographic scales. Strong linkages between the chemistry of regional ozone, fine particles, mercury, and acid deposition have been described above, as well as some common sources and precursors of these pollutants. For example, the combustion of fossil fuels is a major source of NO_x, SO_2, anthropogenic VOCs, primary particulates, mercury, and greenhouse gases. Regional air pollution issues are also linked to problems at the local scale, including "hot spots" near emission sources, and at the global scale, including linkages to climate change. These relationships between pollutants across geographic scales offer opportunities to cost-effectively address multiple problems simultaneously. An important pollution management goal is to develop integrated control strategies incorporating the multiple linkages between pollution problems, the multiple scales over which pollutants cause impacts, the multiple benefits of alternative technology and behavioral choices, and the linkages between air pollution and economic development, energy, agriculture, transportation, and trade policies.

Tremendous progress has been made in understanding air pollution issues and, in many industrialized countries, mitigating the most severe impacts; however, significant scientific uncertainties and challenges still remain. These uncertainties limit our abilities to quantify the frequency and magnitude of transport events on air quality downwind. Some of the most significant scientific uncertainties could be reduced by improving emission characterization, especially in developing countries; further elucidating the

chemistry and physics of secondary pollutant formation, such as organic aerosol formation; and improving our ability to model source-receptor relationships on regional and global scales. Recent advances in satellite monitoring of air pollutants promise to revolutionize the information available to atmospheric scientists, particularly by improving information in areas remote from ground-based measurements (NRC, 2001).

Prioritizing pollutants for control will require developing a better understanding of the various impacts of pollutants on human health and the environment, which include identifying specific toxicological modes of action and synergistic effects of multiple exposures. Long-term risks, such as the increasing concentrations of POPs in humans (passed through generations), may not be recognized until the damage is extensive and difficult to mitigate. Historically, ecosystem impacts have received less attention than human health, although there are often feedbacks to human health and welfare from ecosystem damage. Similarly, the risks associated with potential effects of climate change are now driving science and policy makers to better understand relationships between air pollutants and climate. Improving our ability to quantify the multiple benefits of air pollution control, developing control technologies, and determining cost-optimized control plans will aid policy makers in balancing investments in air pollution control against other economic and development needs.

As industrialized nations in Europe and North America strive to reach stricter domestic air quality standards, the contributions of upwind sources become relatively larger. Consequently, intercontinental transport and increasing global backgrounds of some pollutants will gain attention (Stohl, 2004), as will the growing emissions from developing nations. Industrialized nations can be expected to increasingly engage developing nations in efforts to reduce emissions overseas (Holloway *et al.*, 2003; Keating *et al.*, 2004). However, industrialized nations must first help build fundamental air quality management capacity in developing countries, so they can effectively participate in regional cooperative regimes.

There are a number of mechanisms available for addressing regional air pollution. For example, educating citizens and consumers creates an awareness of the need for cooperative solutions, strengthening the ability of governments to financially commit to control efforts. Educating government leaders about the benefits of pollution control, as well as about the need to invest in building and maintaining cooperative regimes to achieve their own government's environmental goals, may also be affective. Most importantly, experience both within a nation and internationally has demonstrated that the formation of regimes is often necessary for resolving transboundary pollution issues. The process of forming regimes and negotiating agreements often requires significant time and resources. This regime-building process can be smoothed through scientific cooperation between nations, which leads to a shared understanding of the transboundary problem. Building fundamental air quality management capacity in developing countries is necessary so they can effectively participate in regional cooperative regimes. Improving the accessibility and sharing of information on emissions, mitigation options, and impacts of air pollution around the world also aids nations in participating in environmental discussions. Full participation by all affected parties is critical for the success of addressing a regional air quality problem within a regime. Strengthening existing regional and global international institutions, such as the WMO or UNEP's regional centers, may provide a foundation for future cooperative air pollution efforts.

Acknowledgments

The authors would like to acknowledge support from the EPA STAR graduate fellowship program under grant number U915779; from EPA STAR research grants R825821, R831076, and R830960; from a National Aeronautics and Space Administration (NASA) New Investigator Program grant NAG5-12542 to D. Mauzerall; and by award NA17RJ2612 from the National Oceanic and Atmospheric Administration

(NOAA), U.S. Department of Commerce. Any opinions, findings, conclusions, or recommendations expressed in this article are the authors and do not necessarily reflect the views of the U.S. EPA, NASA, or NOAA.

REFERENCES

Ames, R. and Malm, W. (2001). "Comparison of sulfate and nitrate particle mass concentrations measured by IMPROVE and the CDN." *Atmos. Environ.* **35**(5): 905-16.

AMS (2003, Sept. 20, 2004). American Meterological Society. "Acid Deposition." http://www.ametsoc.org/POLICY/aciddepo_2003.html (Accessed: Oct., 2006).

ATSDR (1999). Toxicological Profile for Mercury. Atlanta, GA, Agency for Toxic Substances and Disease Registry. U.S. Department of Health and Human Services, Public Health Service.

Aymoz, G., Jaffrezo, J., Jacob, V., Colomb, A. and George, C. (2004). "Evolution of organic and inorganic components of aerosol during a Saharan dust episode observed in the French Alps." *Atmos. Chem. Phys.* **4**: 2499-512.

Baumgardner, R., Isil, S., Bowser, J. and Fitzgerald, K. (1999). "Measurements of rural sulfur dioxide and particle sulfate: Analysis of CASTNet data, 1987 through 1996." *J. Air. Waste Manag. Assoc.* **49**(11): 1266-1279.

Bell, M., McDermott, A., Zeger, S., Samet, J. and Domenici, F. (2004). "Ozone and short-term mortality in 95 US urban communities:1987-2000." *J. Am. Med. Assoc.* **292**(19): 2372-78.

Bergin, M.S., Russell, A.G., Carter, W.P.L., Croes, B. and Seinfeld, J.H. (1998). VOC Reactivity and Urban Ozone Control. In Encyclopedia of Environmental Analysis and Remediation. J. W. Sons. New York**:** 3355-3383.

Bergin, M.S., Shih, J.-S., Krupnick, A.J., Boylan, J.W., Wilkinson, J.G., Odman, M.T. and Russell, A.G. (2006a). "Regional Air Quality: Local and Interstate Impacts of NOx and SO2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States." *submitted to Environ. Sci. and Technol.*

Bergin, M.S., Shih, J.-S., Krupnick, A.J., Boylan, J.W., Wilkinson, J.G. and Russell, A.G. (2006b). "Regional Air Quality: Local and interstate impacts of NO_x and SO_2 emissions on ozone and fine particulate matter in the Eastern United States." *submitted to Environmental Science and Technology*.

Borrell, P., Builtjes, P., Grennfelt, P. and Hov, O., Eds. (1997). Photo-oxidants, Acidification and Tools:Policy Applications of EUROTRAC Results. Vol. 10. New York, NY, Springer.

Brasseur, G.P., Orlando, J.J. and Tyndall, G.S. (1999). Atmospheric Chemistry and Global Change. New York, Oxford University Press, Inc.

Carter, W.P.L. (1994). "Development of Ozone Reactivity Scales for Volatile Organic Compounds." *Journal of the Air and Waste Management Assoc.* **44**: 881-899.

CDCP (1995). "Children at risk from ozone air pollutions - United States, 1991-1993." *Journal of the American Medical Association* **273**(19): 1484-1485.

Census (2002). U.S. Census Bureau. "Population Estimates". http://eire.census.gov/popest/data/states/tables/NST-EST2003-01.php (Accessed: March, 2004).

Chameides, W. and Cowling, E. (1995a). The state of the Southern Oxidants Study (SOS): policy-relevant findings in ozone pollution research 1988-1994. Coll. Forest Resour. N.C. State Univ., Southern Oxidants Study. Raleigh, N.C. .

Chameides, W.L. and Bergin, M.H. (2002). "Climate change - Soot takes center stage." *Science* **297**(5590): 2214-2215.

Chameides, W.L. and Cowling, E.B. (1995b). The state of the Southern Oxidants Study (SOS): Policy-relevant findings in ozone pollution research 1988-1994. Southern Oxidants Study, North Carolina State University. Raleigh, NC.

Chameides, W.L., Kasibhatla, P.S., Yienger, J. and Levy, H. (1994). "Growth of Continental-Scale Metro-Agro-Plexes, Regional Ozone Pollution, and World Food-Production." *Science* **264**(5155): 74-77.

Chameides, W.L., Luo, C., Saylor, R., Streets, D., Huang, Y., Bergin, M.H. and Giorgi, F. (2002). "Correlation between model-calculated anthropogenic aerosols and satellite-derived cloud optical depths: Indication of indirect effect?" *Journal of Geophysical Research-Atmospheres* **107**(D10).

Chameides, W.L., Yu, H., Liu, S.C., Bergin, M., Zhou, X., Mearns, L., Wang, G., Kiang, C.S., Saylor, R.D., Luo, C., et al. (1999). "Case study of the effects of

atmospheric aerosols and regional haze on agriculture: An opportunity to enhance crop yields in China through emission controls?" *Proceedings of the National Academy of Sciences of the United States of America* **96**(24): 13626-13633.

Clark, W. and Dickson, N., Eds. (2001). Learning to Manage Global Environmental Risks: A Functional Analysis of Social Responses to Climate Change, Ozone Depletion, and Acid Rain. Cambridge, MA, MIT Press.

Cowling, E. (1982). " Acid precipitation in historical perspective." *Environ. Sci. Technol.* **16**: 110A.

DeBell, L., Vozzella, M., Talbot, R. and Dibb, J. (2004). "Asian dust storm events of spring 2001 and associated pollutants observed in New England by the Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) monitoring network." *J. Geophys. Res. Atmos.* **109**(D1): Artic. D01304.

Derwent, R., Collins, W., Johnson, C. and Stevenson, D. (2002). "Global Ozone Concentrations and Regional Air Quality." *Environmental Science and Technology*: A379-A382.

Derwent, R., Stevenson, D., Collins, W. and Johnson, C. (2004). "Intercontinental transport and the origins of the ozone observed at surface sites in Europe." *Atmos. Environ.* **38**: 1891-901.

Driscoll, C., Whitall, D., Aber, J., Boyer, E., Castro, M., Cronan, C., Goodale, C., Groffman, P., Hopkinson, C., Lambert, K., et al. (2003). "Nitrogen Pollution in the Northeastern United States: Sources, Effects, and Management Options." *BioScience* **53**(4): 357-74.

Dutkiewicz, V.A., Qureshi, S., Khan, A.R., Ferraro, V., Schwab, J., Demerjian, K. and Husain, L. (2004). "Sources of fine particulate sulfate in New York." *Atmospheric Environment* **38**(20): 3179-3189.

Dye, T., Roberts, P. and Korc, M. (1995). "Observations of transport processes for ozone and ozone precursors during the 1991 Lake Michigan Ozone Study." *J. Appl. Meteorol.* **34**(8): 1877-89.

EC (2004). Environment Canada. "Mercury and the Environment/Environment and Health/Biogeochemistry". http://www.ec.gc.ca/MERCURY/EH/EN/eh-b.cfm?SELECT=EH (Accessed: Jan., 2005).

EMEP (2004a). Depositions and transboundary fluxes of B[a]P. Detailed information for France for 2004. Meteorol. Synth. Cent.-East (EMEP). http://www.msceast.org/countries/France/index.html

EMEP (2004b). Detailed reports for each EMEP country. Meteorol. Synth. Cent.-East (EMEP). http://www.msceast.org/countries/index.html

EnvCan (2004). Environment Canada. "Mercury and the Environment/Environment and Health/Biogeochemistry". http://www.ec.gc.ca/MERCURY/EH/EN/eh-b.cfm?SELECT=EH (Accessed: Jan., 2005).

EPA (1996). Air Quality Criteria for Ozone and Other Photochemical Oxidants. US Environmental Protection Agency, Off. Res. Dev. Washington, DC.

EPA (1997). Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment. U.S. Environmental Protection Agency, Office of Air Quality Planning & Standards and Office of Research and Development.

EPA (2002a). Air Trends. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. http://www.epa.gov/air/airtrends/highlights.html

EPA (2002b). U.S. Environmental Protection Agency, Office of Air & Radiation, Office of Air Quality Planning & Standards. "Fact Sheet. Health and Environmental Effects of Particulate Matter". http://www.epa.gov/ttn/oarpg/naaqsfin/pmhealth.html (Accessed: Nov., 2006).

EPA (2003). Latest findings on national air quality, 2002 status and trends. US Environmental Protection Agency, Off. Air Qual. Stand. EPA 454/ K-03-001. Research Triangle Park, NC. http://oncampus.richmond.edu□cstevens/EnviroWeb/Documents/USAirQuality2002.pdf

EPA (2004a). Air quality criteria for particulate matter. US Environ. Prot. Agency, Off. Res. Dev. Washington, DC. http://cfpub.epa.gov/ncea/cfm/part matt.cfm

EPA (2004b). EPA Acid Rain Program 2003 Progress Report. U.S. Environmental Protection Agency, Office of Air & Radiation, Clean Air Markets Division. Washington DC.

EPA (2004c). U.S. Environmental Protection Agency. "Mercury". http://www.epa.gov/mercury/index.html (Accessed Nov., 2006).

EPA (2004d). U.S. Environmental Protection Agency. "Pesticides - Persistent Organic Pollutants (POPs)". http://www.epa.gov/oppfead1/international/pops.htm (Accessed: Dec., 2004).

EPA, U.S. (2004e, April 16, 2004). Office of Air and Radiation. "What is Visibility?" http://www.epa.gov/air/visibility/what.html (Accessed: Dec., 2004.

Erisman, J.W., Grennfelt, P. and Sutton, M. (2003). "The European perspective on nitrogen emission and deposition." *Environment International* **29**(2-3): 311-325.

EurComm (2004). "REACH homepage (Registration, Evaluation, Authorisation and Restriction of Chemicals). European Commision". http://europa.eu.int/comm/enterprise/reach/index.htm (Accessed: Oct., 2006).

Falke, S., Husar, R. and Schichtel, B. (2001). "Fusion of SeaWiFS and TOMS satellite data with surface observations and topographic data during extreme aerosol events." *J. Air. Waste Manag. Assoc.* **51**(11): 1579-85.

Farrell, A.E. (2001). "Multi-Lateral Emission Trading: lessons from inter-state NOx control in the United States." *Energy Policy* **29**(13): 1061-1072.

Farrell, A.E. and Keating, T.J. (2002). "Transboundary Environmental Assessments: Lessons From OTAG." *Environmental Science & Technology* **36**(12): 2537-2544.

Fiore, A.M., Jacob, D.J., Bey, R.M., Yantosca, Field, B.D., Fusco, A.C. and Wilkinson, J.G. (2002). " Background ozone over the United States in summer: Origin, trend, and contribution to pollution episodes." *Journal of Geophysical Research-Atmospheres* **107**(D15): 4275.

Galloway, J., Aber, J., Erisman, J., Seitzinger, S., Howarth, R., Cowling, E. and Cosby, B. (2003). "The nitrogen cascade." *BioScience* **53**(4): 341-56.

Gerasopoulos, E., Andreae, M., Zerefos, C., Andreae, T. and Balis, D. (2003). "Climatological aspects of aerosol optical properties in northern Greece." *Atmos. Chem. Phys.* **3**: 2025-41.

Grousset, F., Ginoux, P., Bory, A. and Biscaye, P. (2003). "Case study of a Chinese dust plume reaching the French Alps." *Geophys. Res. Letts.* **30**(6): 1277.

Guodong, Y. (2004). "Environmental Nanomaterials: Occurrence, Syntheses, Characterization, Health Effect, and Potential Applications." *JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH Part A-Toxic/Hazardous Substances & Environmental Engineering* **A39**(10): 2545-2548.

Hillger, D. and Ellrod, G. (2003). "Detection of important atmospheric and surface features by employing principal component image transformation of GOES imagery." *J. Appl. Meteorol.* **42**(5): 611-29.

Hinton, J. and Veiga, M. (2004). Technical and socio-economic profiles of global mercury project sites. In Removal of Barriers to Introduction of Cleaner Artisanal Gold Mining and Extraction Technologies. Vienna, Austria, UN Ind. Dev. Organ. (UNIDO). Global Mercury Project EG/GLO/01/G34. Glob. Environ. Facil./UN Dev. Programme**:** 56pp.

Hogrefe, C., Lynn, B., Civerolo, K., Ku, J.Y., Rosenthal, J., Rosenzweig, C., Goldberg, R., Gaffin, S., Knowlton, K. and Kinney, P.L. (2004). "Simulating changes in regional air pollution over the eastern United States due to changes in global and regional climate and emissions." *Journal of Geophysical Research-Atmospheres* **109**(D22).

Holloway, T., Fiore, A.M. and Hastings, M.G. (2003). "Intercontinental Transport of Air Pollution: Will emerging science lead to a new hemispheric treaty?" *Environmental Science & Technology* **8**(1): 29-43.

Hooper, K. (1999). "EnvirBreast Milk Monitoring Programs (BMMPs): World-Wide Early Warning System for Polyhalogenated POPs and for Targeting Studies in Children's Environmental Health." *Environmental Health Perspectives* **107**(6).

Hooper, K. and McDonald, T.A. (2000). "The PBDEs: An Emerging Environmental Challenge and Another Reason for Breast-Milk Monitoring Programs." *Environmental Health Perspectives* **108**(5).

Horvath, S.M. and McKee, D.J. (1994). Chapter 3. Acute and chronic health effects of ozone. In Tropospheric Ozone: Human Health and Agricultural Impacts. D. J. McKee. Boca Raton, FL, CRC Press/Lewis Publishers**:** 39-83.

Huebert, B.J., Bates, T., Russell, P.B., Shi, G.Y., Kim, Y.J., Kawamura, K., Carmichael, G. and Nakajima, T. (2003). "An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climatic impacts." *Journal of Geophysical Research-Atmospheres* **108**(D23).

Husar, R.B., Tratt, D.M., Schichtel, B.A., Falke, S.R., Li, F., Jaffe, D., Gasso, S., Gill, T., Laulainen, N.S., Lu, F., et al. (2001). "The Asian dust events of April 1998." *J. Geophys. Res.* **106**: 18,317-18,330.

IPCC (2001). Climate Change 2001: Synthesis Report. Summary for Policymakers. Third Assessment. Intergovernmental Panel on Climate Change. http://www.ipcc.ch/

Jacob, D., Logan, J. and Murti, P. (1999). "Effect of rising Asian emissions on surface ozone in the United States." *Geophys. Res. Lett.* **26**(14): 2175-78.

Jacob, D.J., Crawford, J.H., Kleb, M.M., Connors, V.S., Bendura, R.J., Raper, J.L., Sachse, G.W., Gille, J.C., Emmons, L. and Heald, C.L. (2003). "Transport and Chemical Evolution over the Pacific (TRACE-P) aircraft mission: Design, execution, and first results." *Journal of Geophysical Research-Atmospheres* **108**(D20): 1-19.

Jacobson, M.Z. (2002). Atmospheric Pollution: History, Science, and Regulation. Cambridge, Cambridge University Press.

Jaffe, D.A., Anderson, T.L., Covert, D.S., Kotchenruther, R., Troust, B., Danielson, J., Simpson, W., Berntsen, T., Karlsdottir, S., Blake, D.R., et al. (1999). "Transport of Asian air pollution to North America." *Geophys. Res. Letts.* **26**(6): 711-714.

Kaiser, J. (2000). "Evidence Mounts That Tiny Particles Can Kill." *Science* **289**: 22-23.

Keating, T.J., West, J.J. and Farrell, A. (2004). Prospects for international management of intercontinental air pollutant transport. In Intercontinental Air Pollution Transport. A. Stohl. Berlin, Springer. **4 Part G:** 295-320.

Kim, E. and Hopke, P. (2004). "Improving source identification of fine particles in a rural northeastern US area utilizing temperature-resolved carbon fractions." *J. Geophys. Res. Atmos.* **109**(D9): Artic. D09204.

Lelieveld, J., Crutzen, P.J., Ramanathan, V., Andreae, M.O., Brenninkmeijer, C.A.M., Campos, T., Cass, G.R., Dickerson, R.R., Fischer, H., de Gouw, A., et al. (2001). "The Indian Ocean Experiment: Widespread air pollution from South and Southeast Asia." *Science* **291**: 1031-1036.

Levy, J.I., Carrothers, T.J., Tuomisto, J.T., Hammitt, J.K. and Evans, J.S. (2001). "Assessing the public health benefits of reduced ozone concentrations." *Environ. Health Perspect.* **109**: 9-20.

Levy, M.A. (1994). European Acid Rain: The Power of Tote-Board Diplomacy. In Institutions for the Earth: Sources of Effective International Environmental Protection. P. M. Haas, R. O. Keohane and M. A. Levy. Cambridge, MA, MIT Press.

Li, Q.B., Jacob, D.J., Bey, I., Palmer, P.I., Duncan, B.N., Field, B.D., Martin, R.V., Fiore, A.M., Yantosca, R.M., Parrish, D.D., et al. (2002). "Transatlantic transport of pollution and its effects on surface ozone in Europe and North America." *Journal of Geophysical Research-Atmospheres* **107**(D13).

Little, M. (2002). "Reducing Mercury Pollution from Electric Power Plants." *Issues in Science and Technology* (Summer).

Liu, W., Hopke, P. and VanCuren, R. (2003). "Origins of fine aerosol mass in the western United States using positive matrix factorization." *J. Geophys. Res. Atmos.* **108**(D23): Artic. 4716.

Mauzerall, D. and Wang, X. (2001). "Protecting agricultural crops from the effects of tropospheric ozone exposure." *Annu. Rev. Energy Environ.* **26**: 237-68.

McLaughlin, S.B. and Downing, D.J. (1995). "Interactive Effects of Ambient Ozone and Climate Measured on Growth of Mature Forest Trees." *Nature* **374**(6519): 252-254.

Menon, S.H., James; Nazarenko, Larissa; Yunfeng Luo (2002). "Climate Effects of Black Carbon Aerosols in China and India." *Science* **297**(5590): 2250-2254.

Munthe, J. and Palm, A. (2003). Atmospheric Cycling of Mercury and Persistent Organic Pollutants. Chap. 10. EUROTRAC-2, subproject MEPOP. http://www.gsf.de/eurotrac/publications/et2_fin_rep/fr_10_mepop.pdf

NARSTO (2000). An Assessment of Tropospheric Ozone - A North American Perspective. North American Research Strategy on Tropospheric Ozone. Published by the Electric Power Research Institute, Report 100040. Palo Alto, CA.

NARSTO (2003). Particulate matter science for policy makers. North American Research Strategy on Tropospheric Ozone. Published by the Electric Power Research Institute, Report 1007735. Palo Alto, CA.

NRC (1991). Rethinking the Ozone Problem in Urban and Regional Air Pollution. Washington, D.C., National Research Council, National Academy Press.

NRC (2000). Toxicological Effects of Methylmercury. Washington, D.C., National Research Council, National Academy Press.

NRC (2001). Global Air Quality: An Imperative for Long-term Observational Strategies. Washington, D.C., National Research Council, National Academy Press.

NRC (2003). Managing Carbon Monoxide in Meteorological and Topographical Problem Areas. . Washington, DC, National Research Council, National Academy Press.

NRC (2004). Air Quality Management in the United States. Washington D.C., National Research Council, National Academy Press.

Odman, M.T., Boylan, J.W., Wilkinson, J.G. Russell, A.G., Mueller, S.F., Imhoff, R.E., Doty, K.G., Norris, W.B., McNider, R.T. (2002). SAMI Air Quality Modeling Final Report. Southern Appalachian Mountains Initiative (SAMI) Governing Body. Ashville, NC.

Ostrom, E. (1990). Governing the Commons: The Evolution of Institutions for Collective Action. New York, Cambridge University Press.

Pacyna, J.M., Pacyna, E.G., Steenhuisen, F. and Wilson, S. (2003). "Mapping 1995 global anthropogenic emissions of mercury." *Atmospheric Environment* **37**(Supplement 1): 109-117.

Pal, B. and Ariya, P. (2004). "Gas-phase HO center dot-initiated reactions of elemental mercury: kinetics, product studies, and atmospheric implications." *Environ. Sci. Technol.* **38**(21): 5555-66.

Park, R.J., Jacob, D.J., Field, B.D., Yantosca, R.M. and Chin, M. (2004). "Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy." *J. Geophys. Res.* **109**(D15).

Parrish, D., Holloway, J., Trainer, M., Murphy, P., Forbes, G. and Fehsenfeld, F. (1993). "Export of North America ozone pollution to the North Atlantic Ocean." *Science* **259**: 1436-39.

Pekkanen, J. and Kulmala, M. (2004). "Exposure assessment of ultrafine particles in epidemiologic time-series studies." *Scandinavian Journal of Work Environment & Health* **30**: 9-18.

Penner, J.E., Andreae, M., Annegarn, H., Barrie, L., Feichter, J., Hegg, D., Jayaraman, A., Leatich, R., Murphy, D., Nganga, J., et al. (2001). Aerosols: Their Direct and Indirect Effects. In Climate change 2001: The scientific basis: Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change. J. T. Houghton, Y. DIng, D. J. Griggset al. Cambridge, UK, Cambridge Univ. Press.

Perry, K.D., Cahill, T.A., Eldred, R.A., Dutcher, D.D. and Gill, T.E. (1997). "North african dust to the eastern United States." *Journal of Geopyhsical Research* **102**: 11225-11238.

Pope, C.A. (2004). "Air pollution and health - Good news and bad." *New England Journal of Medicine* **351**(11): 1132-1134.

Pope, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K. and Thurston, G.D. (2002). "Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution." *Jama-Journal of the American Medical Association* **287**(9): 1132-1141.

Prather, M., Gauss, M., Berntsen, T., Isaksen, I. and Sundet, J. (2003). "Fresh air in the 21st century?" *Geophys. Res. Lett.* **30**(2): Artic. 1100.

Prinn, R.G. (2003). "The cleansing capacity of the atmosphere." *Annu. Rev. Environ. Resour.* **28**: 29-57.

Prospero, J.M. (1999). "Long-term measurements of the transport of African mineral dust to the southeastern United States: Implications for regional air quality." *Journal of Geophysical Research-Atmospheres* **104**(D13): 15917-15927.

Querol, X., Alastuey, A., Ruiz, C.R., Artinano, B., Hansson, H.C., Harrison, R.M., Buringh, E., ten Brink, H.M., Lutz, M. and Bruckmann, P. (2004). "Speciation and origin of PM10 and PM2.5 in selected European cities." *Atmospheric Environment* **38**(38): 6547-6555.

Ranzieri, A. and Thullier, R. (1991). San Joaquin Valley air quality study (SJVAQS) and atmospheric utility signatures, predictions, and experiments (AUSPEX): a collaborative modeling program. The Air and Waste Management Assoc., 84th Annual Meeting and Exhibition, Vancouver, Canada.

Renner, R. (2004). "Rethinking atmospheric mercury." *Environ. Sci. Technol. (Online News, Science News).*

RIVM (1995). National Institute for Public Health and the Environment (RIVM). Bilthoven, The Netherlands. "NO_x and SO_2 from anthropogenic sources in 1995, dataset EDGARV32". http://www.rivm.nl/edgar/model/ims/ (Accessed: Dec., 2004).

Rodan, B. (2002). The Foundation for Global Action on Persistent Organic Pollutants: A United States Perspective. Washington, DC, EPA#600P02003f. 167 pp. US Environ. Prot. Agency, Off. Res. Dev.

Rodhe, H., Dentener, F. and Schulz, M. (2002). "The global distribution of acidifying wet deposition." *Environ. Sci. Technol.* **36**: 4382-88.

Rogers, C.M. and Bowman, K.P. (2001). "Transport of smoke from the Central American fires of 1998." *Journal of Geophysical Research* **106D**(22): 28357-28368.

Ryaboshapko, A., Bullock, R., Ebinghaus, R., Ilyin, I., Lohman, K., Munthe, J., Petersen, G., Seigneurd, C. and Wangberg, I. (2002). "Comparison of mercury chemistry models." *Atmos Env.* **36**: 3881-3898.

Rypdal, K., Berntsen, T., Fuglestvedt, S., Aunan, K., Torvanger, A., Stordal, F., Pacyna, J.M. and Nygaard, L.P. (2005). "Ozone and aerosols in future climate agreements: scientific and political challenges." *Environmental Science & Policy* **8**(1): 29-43.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P. and Scott, C. (2004). "Global Source Attribution for Mercury Deposition in the United States." *Environmental Science & Technology* **38**: 555-569.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., Scott, C. and Levin, L. (2003). "Simulation of the fate and transport of mercury in North America." *J. Physique.* **107**: 1209-12.

Seinfeld, J.H. and Pandis, S.N. (1998). Atmospheric Chemistry and Physics. New York, John Wiley & Sons, Inc.

Shia, R.L., Seigneur, C., Pai, P., Ko, M. and Sze, N.D. (1999). "Global simulation of atmospheric mercury concentrations and deposition fluxes." *Journal of Geophysical Research-Atmospheres* **104**(D19): 23747-23760.

Shih, J.-S., Bergin, M.S., Krupnick, A. and Russell, A.G. (2003). Controlling Ozone and Fine Particulates: Cost Benefit Analysis with Meteorological Variability. Discussion Paper 03–55, Resources For the Future. Washington, D.C.

Sister, J. and Malm, W. (2000). "Interpretation of trends of PM2.5 and reconstructed visibility from the IMPROVE network." *J. Air. Waste Manag. Assoc.* **50**(5): 775-89.

Solomon, G. and Mahalingaiah, S. (2001). Persistent Organic Pollutants: Human Health Issues. Center for Health and the Global Environment, Harvard Medical School. http://www.med.harvard.edu/chge/textbook/toxic/organic/transcript.htm

Sommar, J., Gardfeldt, K., Stromberg, D. and Feng, X. (2001). "A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury." *Atmos. Environ.* **35**(17): 3049-54.

Stieb, D., Judek, S. and Burnett, R. (2003). "Meta-analysis of time-series studies of air pollution and mortality: update in relation to the use of generalized additive models." *J. Air. Waste Manag. Assoc.* **53**: 258-61.

Stohl, A., Ed. (2004). Intercontinental Transport of Air Pollution. New York, NY, Springer-Verlag.

Takemura, T., Uno, I., Nakajima, T., Higurashi, A. and Sano, I. (2002). "Modeling study of long-range transport of Asian dust and anthropogenic aerosols from East Asia." *Geophys. Res. Letts.* **29**(24): 2158.

Tanner, R.L., Parkhurst, W.J., Valente, M.L., Humes, K.L., Jones, K. and Gilbert, J. (2001). "Impact of the 1998 CentralAmerican fires on PM2.5 mass and composition in the southeastern United States." *Atmospheric Environment* **35**: 6539–6547.

Tingey, D.T., Olszyk, D.M., Herstrom, A.A. and Lee, E.H. (1994). Chapter 6. Effects of Ozone on Crops. In Tropospheric Ozone: Human Health and Agricultural Impacts. D. J. McKee. Boca Raton, FL, CRC Press/Lewis Publishers**:** 175–206.

UNEP (2001). UNEP Stockholm Convention on POPs, United Nations Environment Programme.

UNEP (2003). Chemicals program: Global Mercury Assessment Report. United Nations Environment Program. Geneva, Switz. http://www.chem.unep.ch/mercury/

UNEP (2004). United Nations Environment Program. "Chemicals: Persistent Organic Pollutants (POPs)." http://www.chem.unep.ch/pops/ (Accessed: Sept., 2004).

USGS (2000). Mercury in the Environment. Fact Sheet 146-00, United States Geological Survey.

VanCuren, R.A. and Cahill, T.A. (2002). "Asian aerosols in North America: Frequency and concentration of fine dust." *Journal of Geophysical Research* **107**(D24): 4804.

VanDeveer, S.D. (2005). European politics with a scientific face: Framing, national participation, and capacity in LRTAP. In Assessments of Regional and Global Environmental Risks: Designing Processes for Effective Use of Science in Decisionmaking. A. Farrell and J. Jaeger. Washington, DC, RFF Press.

West, J.J., Osnaya, P., Laguna, I., Martinez, J. and Fernandez, A. (2004). "Co-control of urban air pollutants and greenhouse gases in Mexico City." *Environmental Science & Technology* **38**: 3474-3481.

WHO (2003). World Health Organization. Bonn, Germany. "Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide". http://www.euro.who.int/document/e79097.pdf (Accessed: Nov., 2004).

WHO (2004). World Health Organization. "Children's environmental health: Outdoor Air Pollution". http://www.who.int/ceh/risks/cehair/en/ (Accessed: Nov., 2004).

Wolff, G. and Lioy, P. (1980). "Development of an ozone river associated with synoptic scale episodes in the eastern United States." *Environ. Sci. Technol.* **14**: 1257- 60.

WorldBank (2004). "Persistent organic pollutants". http://lnweb18.worldbank.org/ESSD/envext.nsf/50ByDocName/WhatArePOPs (Accessed: Nov., 2004).

Wotama, G. and Trainer, M. (2000). "The influence of Canadian forset fires on pollutant concentrations in the United States." *Science* **288**: 324-328.

Yienger, J.J., Galanter, M., Holloway, T.A., Phadnis, M.J., Guttikunda, S.K., Carmichael, G.R., Moxim, W.J. and Levy, H. (2000). "The episodic nature of air pollution transport from Asia to North America." *Journal of Geophysical Research-Atmospheres* **105**(D22): 26931-26945.

Young, O.R., Ed. (1999). The Effectiveness of International Environmental Regimes: Causal Connections and Behavioral Mechanisms. Global Environmental Accord: Strategies for Sustainability and Institutional Innovation. Cambridge, MIT Press.

CHAPTER 6

CONCLUSIONS AND FUTURE RESEARCH

This thesis presents a unified study of regional air pollution and results from photochemical modeling applications for transboundary policy development and support. In this chapter, findings of the modeling applications and research collaborations are summarized with recommendations for future research.

6.1 Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States

The effects of emissions reductions from three source categories in each of 18 states and 4 grouped sets of states on subsequent levels of ozone and secondary $PM_{2.5}$ in each state were evaluated over three meteorological episodes. The emissions categories evaluated are total SO_2, ground-level NO_x, and elevated NO_x. The summer episode (July) had the highest concentrations of both ozone and $PM_{2.5}$. Emissions of SO_2 are found to be largely responsible for $PM_{2.5}$ concentrations, and emissions of ground-level NO_x are found to be largely responsible for ozone concentrations. An average of 77% of each state's ozone and $PM_{2.5}$ concentrations that are sensitive to the emissions evaluated here are found to be caused by emissions from other states. Delaware, Maryland, New Jersey, Virginia, Kentucky, and West Virginia are shown to have high concentrations of ozone and $PM_{2.5}$ caused by interstate emissions. When weighted by population, New York receives greatly increased contributions to these pollutants from other states. When accounting for emission rates, combined states from the western side of the modeling domain and individual states such as Illinois, Tennessee, Indiana, Kentucky, and Georgia are major contributors to interstate ozone. Ohio, Indiana, Tennessee, Kentucky, and Illinois are the major contributors to interstate $PM_{2.5}$. When considering an equivalent

mass of emissions, Tennessee, Kentucky, West Virginia, Virginia, and Alabama appear to cause a significant fraction of these pollutants in other states. A companion study (Shih et al., need full ref) utilizes the results of this analysis to identify least-cost utility NO_x emissions controls for optimal ozone reduction.

- **Future Research**: More specific potential control strategies should be identified by extending the economic analysis associated with this study to include major components of ground level NO_x (e.g. mobile sources) and elevated SO_2 emissions that could be reduced using current technologies having known costs and emissions reduction capabilities. The analysis should address additional impacts of control options such as changes in emissions of greenhouse gases (e.g. methane and carbon dioxide), mercury, or other pollutants. A similar source-receptor analysis should be performed defining receptor areas by variables other than political boundaries, such as concentration threshold exceedances or population densities, to identify more efficient control options. Higher-order sensitivity analysis should be performed to ensure that non-linearities do not impact the relative results. As modeling of secondary organic aerosols becomes more reliable, emission source categories contributing to this important component of $PM_{2.5}$ should also be included. Additional episodes should be evaluated, preferably with a Classification and Regression Tree (CART) analysis to quantify interstate emissions contributions to annual $PM_{2.5}$ concentrations (categorizing or 'binning' modeled days with characteristics similar to observed days and using weighting to represent a full year).

6.2 Single-Source Impact Analysis Using 3D Air Quality Models

Results presented here demonstrate the use of two 3D photochemical air quality models using first and second order DDM and B-F for nonlinear, long-range evaluation of single-source emissions impacts for use in regional air quality management applications. Excess NO_x emissions from the Sammis power-plant in Stratton, Ohio are

predicted to have increased maximum one-hour averaged ozone concentrations over a large region, including increases greater than 0.5 ppbv in Ohio, Pennsylvania, Maryland, New York, West Virginia, Virginia, and North and South Carolina. Simulated peak maximum one-hour averaged concentrations are found to have increased up to 2.3 ppbv. The excess emissions from the Sammis plant are also shown to cause some reductions in maximum hourly ozone concentrations. The maximum ozone increases are compared with maximum decreases for the August period using second-order DDM, and are found, in aggregate, to be greater in magnitude by 42%. When evaluated during hours of elevated ozone concentrations (greater than 0.060 ppm), the maximum increases in ozone are higher than decreases by 82% and the spatial extent of exacerbation is more than double that of depression.

While these calculated ozone sensitivities are low, the spatial distributions are large, and cumulative impacts from single-sources are high and increasing worldwide. Techniques are needed to characterize contributions to pollutants from large individual sources in order to design and enforce air quality control strategies. While influenced by uncertainties, model assessments such as this one, in conjunction with ambient measurements and controlled experiments, are the most scientifically based methods available for predicting and learning about the dynamic and integrated system of emissions and secondary pollutants, and provide useful guidance for the design of efficient air quality control programs.

- **Future Research**: An application comparison with currently available plume-in-grid models would be beneficial to both plume-in-grid model developments as well as for analysis of the effects of plume dispersion in the Eulerian models. Sensitivity of results to the vertical grid resolution of the model and to emissions characteristics such as temperature, velocity, and stack-height should be evaluated. Simulations of impacts of emissions from other large power-plants on regional, multi-day ozone concentrations

would provide comparative predictions to previous field studies of power-plant plumes that indicate important differences in the ozone production efficiency of individual power-plant plumes based on plume size and ambient conditions, providing guidance on design options such as capacity and location of new plants.

6.3 Impacts of Volatile Organic Compounds on Air Quality and the Development and Expansion of Regulatory Applications Accounting for their Ozone Formation Potentials

The collaborative nature of the research program described here has been a major factor in the success of the development of a regulatory strategy of accounting for reactivity in the control of volatile organic compounds. Section 1 of this chapter includes a publication for the solvent industry providing information directly related to the atmospheric impacts of emissions from solvent use and manufacture. Section 2 of this chapter describes reactivity quantification measures and how uncertainties and environmental variability were addressed in developing scales applicable for regulatory use. Results from a regional evaluation of reactivity using DDM are presented, showing that the relative ranking of MIR based metrics were fairly consistent with results from previous modeling studies. These results provide a foundation for reactivity based regulations in a number of states where reactivity was not previously quantified, as well as for regulations on a regional scale. Current and upcoming regulations accounting for reactivity include Reactivity Adjustment Factors for alternatively fueled vehicles and aerosol coatings regulations in California, and a cap-and-trade emissions program for highly reactive VOCs from industrial sources in the Houston- Galveston-Brazoria area of Texas. In addition, the U.S. EPA has issued guidance encouraging the consideration of reactivity in SIP development where relevant, and the Reactivity Research Working Group has coordinated research addressing barriers to the application of reactivity based regulations on the regional scale.

Future Research: Now that the technical evaluation of reactivity is fairly well established, and several regulatory applications are in place, efforts should be made to identify other areas where reactivity accounting in VOC emissions control can provide more effective and efficient ozone reduction than under current policies. Accurate, speciated inventories of VOC emissions are necessary for this activity. The potential contributions to ozone formation from radical-forming compounds other than VOCs should be investigated, as those compounds could be included with organics in reactivity based ozone control strategies. Based on concentration levels of reactive VOCs in emissions inventories, the effect of the magnitude of compound perturbation on reactivity measures should also be evaluated. The Reactivity Research Working Group is well positioned to extend coordination efforts to research focused on identifying the sources of organic compounds contributing to secondary organic aerosols and for framing a regulatory approach to controlling this pollutant constituent. As described in Chapter 5, building cooperative regimes is an intensive, lengthy process. The relationships between participating parties in the RRWG are well established, and many parties impacted by potential regulation of organic emissions are members.

6.4 Regional Atmospheric Pollution and Transboundary Air Quality Management

This section demonstrates the integrated nature of regional atmospheric pollution, the widespread and extensive damage caused by these pollutants, and the need for political cooperation in mitigating the impacts. In particular, collaborations involving all impacted parties must be built on a foundation of trust and common understanding of the issues, which are greatly facilitated through scientific cooperation. Building the technical capacity of impacted parties also results in the development of more efficient strategies and in greater cooperation in compliance. As we begin to understand and experience the

cumulative effects of over a century of large scale anthropogenic emissions, we can learn from and build upon structures we have already established for addressing previous air pollution issues to create adaptable, responsive approaches to transboundary atmospheric management.

APPENDICES

Appendix A.

Supplemental Information to Chapter 2. Regional Air Quality: Local and Interstate Impacts of NO_x and SO_2 Emissions on Ozone and Fine Particulate Matter in the Eastern United States

A1. Model Description and Data Inputs

A2. Model Performance

- A2.1. Ozone
- A2.2. Aerosols

A3. Results

- A3.1. States as sources
  - (a) Ozone SRCs
  - (b) $PM_{2.5}$ SRCs
  - (c) Spatial and population weighted local and regional SRIFs
- A3.2. States as receptors
  - (a) Ozone spatial and population weighted SRIFs, May episode
  - (b) Ozone SRIF receptors
  - (c) Ozone SRC receptors
  - (d) $PM_{2.5}$ SRC receptors

A4. References

A1. Model Description and Data Inputs

A1.1 Additional details on model description. URM-1ATM solves the atmospheric diffusion equation (ADE; Equation A1) using finite elements over a variable scale grid by calculating the change in concentration of species *i* with time,

$$\frac{\partial c_i}{\partial t} + \nabla \bullet (\mathrm{u} c_i) = \nabla \bullet (\mathrm{K} \nabla c_i) + R_i + E_i \qquad \text{(A1)}$$

where **u** is a velocity field, **K** is the diffusivity tensor, R_i represents chemical reactions of species *i* with all other species, and E_i represents net sources of species *i* not accounted for in the boundary conditions. A multiscale approach (Odman and Russell, 1991) is used to capture the physicochemical dynamics while reducing the computational load. The vertical grid has 7 non-uniform layers, with the thinnest layer near the ground and the layers thickening with increasing altitude. This vertical scheme allows detailed treatment of ground level sources and best represents ground level mixing and deposition processes, capturing diurnal changes in mixing depths and multi-day transport events.

A1.2 Additional details on treatment of aerosols and clouds. Primary and secondary particulate matter are segregated in three groups: inert species (magnesium, potassium, calcium, elemental carbon [EC], and 'other'); inorganic ionic species (sulfate, nitrate, ammonium, sodium, chloride, and hydrogen ion); and organic carbon (OC). These transported aerosol species are segregated into four size bins with aerometric diameters of: $d < 0.156$ μm; $0.156 \leq d < 0.625$ μm; $0.625 \leq d < 2.5$ μm; and $2.5 \leq d < 10.0$ μm. Primary particle emissions vary by source depending on species and size. Condensation and evaporation cause mass transfer and particle growth between gas and aerosol species (Pandis *et al.*, 1993). Inorganic gas-aerosol partitioning is calculated using ISORROPIA,

a thermodynamic equilibrium model assuming an internally mixed aerosol (Nenes *et al.*, 1998). Secondary organic aerosols are produced from gas phase reactions using lumped experimental and estimated organic aerosol yields (Pandis *et al.*, 1992), and account for roughly a quarter of the mass of $PM_{2.5}$. However, many uncertainties still exist in our understanding of the formation, effects, and composition of secondary organic aerosols, so the sensitivity of this component of $PM_{2.5}$ to emissions is not examined in this study. URM-1ATM incorporates the Reactive Scavenging Module (RSM) (Scott, 1987; Berkowitz *et al.*, 1989) to account for heterogeneous reactions, convective cloud processes, and pollutant scavenging. Particle deposition rates depend on size, atmospheric turbulence, and surface characteristics.

A1.3 Additional details on model inputs. The Regional Atmospheric Modeling System (RAMS) (Pielke *et al.*, 1992; Odman, 2002b) is applied in a nonhydrostatic mode, including cloud and rain microphysics, to provide spatially and temporally resolved meteorological fields. Three nested grids were used for simulations, which were then interpolated to the URM-1ATM multiscale grid. The RAMS thirty-one layer vertical structure results were aggregated to the seven URM-1ATM layers. The RAMS grid configuration matched the URM horizontal domain extent and the upper boundary altitude of 12,867 meters.

Gridded, hourly, day-specific emissions were estimated using the Emissions Modeling System (EMS-95) (Wilkinson *et al.*, 1994). Emissions from elevated point sources are injected hourly in the appropriate vertical layer determined by the height of the emissions stack and the emissions temperature and velocity. Continuous Emission Monitor data is incorporated where available. Ground level sources are incorporated as surface boundary conditions and include on-road and off-road mobile sources, biogenic sources, low-level point sources, and anthropogenic area sources. MOBILE5b (EPA, 1994), which is incorporated into EMS-95, was used to model vehicle-dependent

emissions factors of CO, NO_x, and total organic gases. MOBILE5b emissions factors were coupled with data on vehicle miles traveled and vehicle mix by state, county, and roadway type; and speeds by vehicle and roadway type to estimate emissions. Biogenic emissions were estimated using the U.S. EPA Biogenic Emissions Inventory System-2 (BEIS2) (Pierce, 1990; Pierce, 1996a; Pierce, 1996b) as a function of the spatially and temporally resolved temperature and solar radiation. Emissions estimates from mobile sources were also calculated as a function of temperature. Foundation data for point, area, and on-road mobile source emissions were developed by Pechan/Avanti (Pechan, 2001), and point source emissions estimates for major utilities in the domain were refined using utility-provided day specific data.

A2. Model Performance

A2.1. Ozone

Measurements from the US EPA Aerometric Information Retrieval System (AIRS) (EPA, 2001) are used to evaluate ozone model performance in this study, following performance guidelines for urban-scale ozone modeling from the US EPA (EPA, 1991). Ozone measurements from AIRS monitors located in areas represented by simulation cells of 24x24 km and 48x48 km were compared with the model concentration predictions in those cells. Concentrations from 48x48 km cells were calculated for 24x24 km cells using bilinear interpolation with neighboring cell values, and these interpolated values were used in the performance calculations.

Mean Normalized Bias (MNB) and Mean Normalized Error (MNE) were calculated as:

$$MNB_{O3} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left(c_i^m - c_i^o\right)}{c_i^o}\times 100\% \quad \text{(A1a)}$$

$$MNE_{O3} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|c_i^m - c_i^o\right|}{c_i^o}\times 100\% \quad \text{(A1b)}$$

In these equations, *N* is the total number of hourly measured-predicted concentration pairs where observed ozone concentrations are greater than 40 ppb, *c* is concentration, *o* is observed concentration, and *m* is modeled concentration. The average MNB_{O3} and MNE_{O3} (Table A1) are well within the EPA guidelines for urban scale modeling, which are MNB within ±15% and MNE<35% (EPA, 1991). Overall, averaged daily MNB_{O3} results are slightly positive, indicating general over-prediction, and are slightly lower for the July episode (+1.6%) than the May episode (+3.2%). The daily maximum is +13%

(over-predicted) on July 17, and the daily minimum is -6% (under-predicted) on both July 14 and May 24. The averaged daily MNE_{O3} results are slightly better for May (16.8%) than for July (21.4%), with a daily maximum of 27% on July 16. No less than 2,200 hourly measured-predicted concentration pairs were used for any day (i.e., *N* in Equations A1a and A1b), with an average of 5,677 hourly measured-predicted concentration pairs per day used during the July episode and 3,272 hourly measured-predicted concentration pairs used during the May episode.

A2.2. Aerosols

While our understanding of aerosol science, quality and quantity of ambient measurements, and modeling capabilities are rapidly advancing, modeling of atmospheric $PM_{2.5}$ is in an earlier stage of development as compared to ozone modeling, and relatively few measurements are currently available for performance evaluation. Available measurements during these episodes are sparse and collected in 24-hour increments. Additionally, most aerosol measurement sites active during the simulated periods are located in rural areas. Results from an observational network and a measurement study are used for model performance evaluation of sulfate and $PM_{2.5}$ predictions. Measurements are used from stations whose locations are within cells of 24x24 or 48x48 km.

The Interagency Monitoring of Protected Visual Environments (IMPROVE) network (NPS, 1995) provides 24-hour averaged, speciated data taken on Wednesday and Saturday of each week during both of our performance episodes, giving us 5 days for aerosol model performance evaluation. This IMPROVE network includes 11 sites that are within 24x24 or 48x48 km simulation cells, all of which report data for the July episode, and 10 of which report data for the May episode. A smaller study was conducted in the New England area (Salmon, 1999), providing measurements in NY and MA on July 14, 1995 from 5 sites, referred to as the ‘Cass sites’.

Twenty-four hour averaged $PM_{2.5}$ concentrations at the IMPROVE and Cass sites are compared with model predictions (Figure A.1). Three values are shown: measured $PM_{2.5}$; reconstructed $PM_{2.5}$; and modeled $PM_{2.5}$. Reconstructed $PM_{2.5}$ is calculated using only the identified species mass. Much of the unidentified mass in measured $PM_{2.5}$ is thought to be water (Andrews *et al.*, 2000) and elements heavier than carbon (mostly oxygen and nitrogen) that are part of the organic aerosol. Particle bound water and unidentified species are not included in the modeled $PM_{2.5}$ calculation, so reconstructed $PM_{2.5}$ is a more accurate performance target for model predictions.

The model follows the high and low concentration days from the IMPROVE measurements well, and also largely represents the spatial trend of concentration for both the IMPROVE and Cass sites, as shown by high and low predictions at sites with high and low measurements, respectively. With some exceptions, the total aerosol concentrations agree well, though model values tend to be below measured concentrations. Canadian point sources were not available for this study, and recent inventory analysis suggest that the Canadian area source emissions are underestimated (Wilkinson, 2006) , which may cause much of the under-prediction at the Cass sites.

To quantify the overall aerosol performance, the Mean Fractional Error (MFE_{ar}) and Mean Fractional Bias(MFB_{ar}) for measured $PM_{2.5}$ and reconstructed $PM_{2.5}$ are calculated from the IMPROVE sites (Equation A2, Table A.2). These performance metrics, recommended by Boylan and Russell (Boylan and Russell, 2006) are calculated differently from MNB_{O3} and MNE_{O3}, for a number of reasons. The number of measurements (N) is small as compared with ozone measurements, and there is no cutoff concentration applied. Aerosol measurements have a greater uncertainty than ozone measurements, which is better represented by these calculations which do not assume that the observations are the truth. The maximum bias and error are bounded (MFB ranges from −200% to +200% and MFE ranges from 0% to +200%), and do not allow a few data points to dominate the metric. Finally, the metrics are symmetric, giving equal weight,

on a relative basis, to concentrations whether they are simulated higher or lower than observations.

$$MFB_{ar} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left(c_i^m - c_i^o\right)}{\frac{1}{2}\left(c_i^m + c_i^o\right)} \times 100\% \quad \text{(A2a)}$$

$$MFE_{ar} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|c_i^m - c_i^o\right|}{\frac{1}{2}\left(c_i^m + c_i^o\right)} \times 100\% \quad \text{(A2b)}$$

MFB_{ar} tends to be negative for $PM_{2.5}$ (i.e. generally indicating under-prediction), ranging from +19 to -43% for each day, and is -21% when all days are considered. This is expected as the simulated value does not include water. Considering only reconstructed measured $PM_{2.5}$, the bias is typically low and positive, +6% including all days, except for May 27 when it is +36%. Overall, the MFE_{ar} is 35% for total $PM_{2.5}$, and 30% for reconstructed $PM_{2.5}$.

One possible contributing factor to this slight general over-prediction of PM2.5 is that the reported organic fraction of measured $PM_{2.5}$ is actually organic carbon (OC) multiplied by a conversion factor of 1.4 to account for likely associated hydrogen and oxygen. A more recent recommendation for this conversion factor is 1.6 for urban areas and 2.1 for rural areas (Turpin and Lim, 2001). Organic aerosol accounts for roughly a quarter of $PM_{2.5}$ mass, suggesting that measured $PM_{2.5}$ may be slightly under-estimated, reducing this positive modeling bias. Modeling of OC is still highly uncertain, however model performance results for this study were very good (Table A.2), with an overall MFB of +15% and MFE of 40%. Of note, the companion modeling study for this project resulted in an overall under-prediction of OC (Boylan *et al.*, 2006).

Sulfate is the largest single component of $PM_{2.5}$ for most sites from both IMPROVE and Cass sites if unidentified species from the Cass study are not considered, particularly on days with high $PM_{2.5}$ concentrations. Organic aerosols tend to be the next most common component; however its characterization still has significant uncertainties.

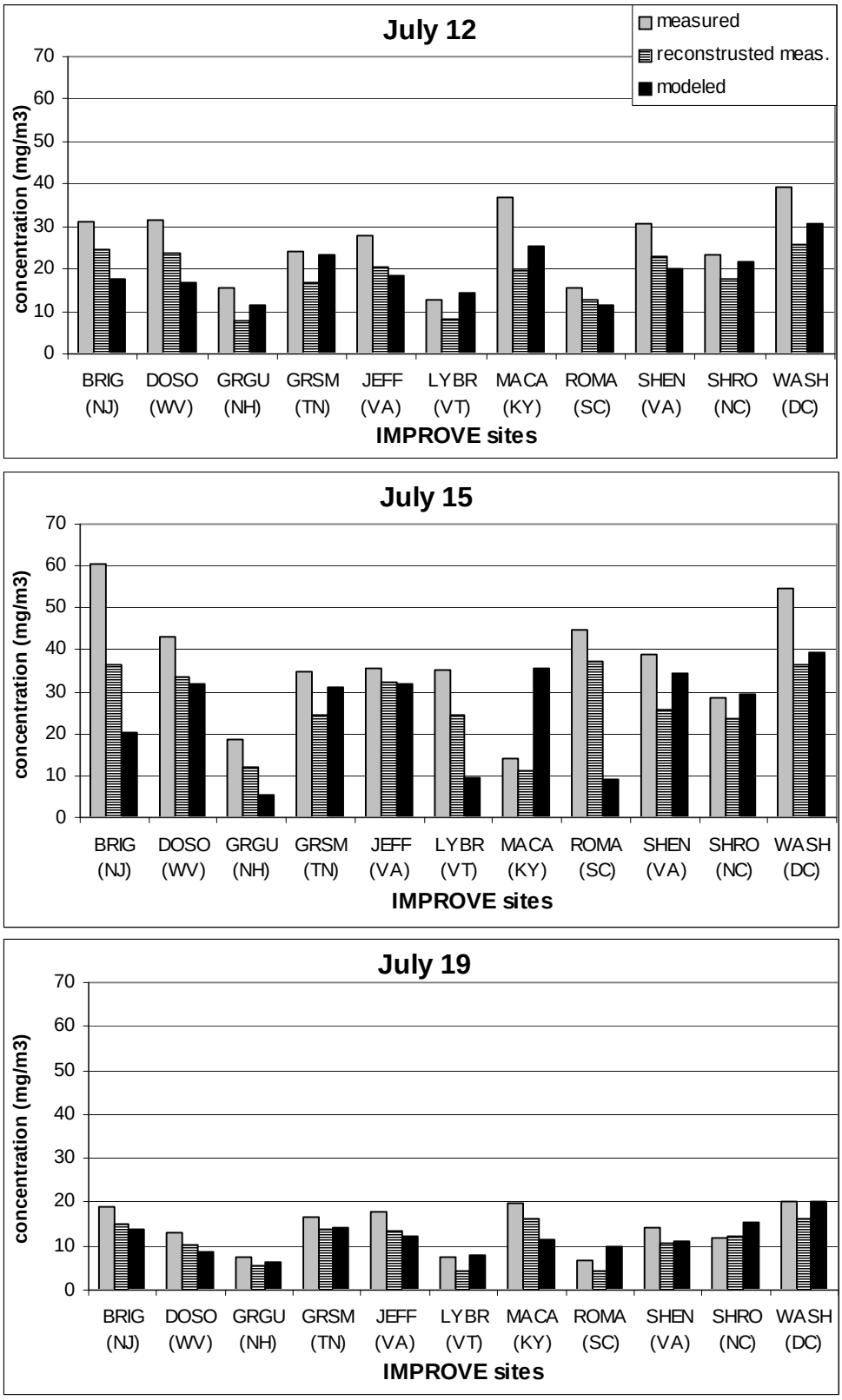
Because sulfate is such an important component of $PM_{2.5}$ and is impacted by the emissions controls evaluated in this study, a comparison of sulfate measurements and predictions is presented (Figure A.2). As can be seen, high and low sulfate days are generally well represented, as is the spatial trend of the concentrations. A few IMPROVE sites show the model either over-predicting (MACA) or under-predicting (ROMA, LYBR) observations made on July 15. The July 14 Cass sites are all under-predicted, however the spatial trend of concentrations is captured. As mentioned above, the underestimated Canadian emissions are likely the cause of much of the under-prediction. Over the 5 IMPROVE days, the MFB_{ar} for sulfate ranges from 39% to -18%, and is 0% over all days combined. The MFE is 40% overall (Table A.2). Additional performance information for these episodes from a related URM-1ATM application is available elsewhere (Boylan *et al.*, 2006).

Table A.1. Mean Normalized Bias and Mean Normalized Error of ozone predictions (%). Every hour-averaged measurement was used if the ozone concentration was greater than 40 ppb and the location coincided with a 24x24 or 48x48 km modeling cell. 497 sites contributed to the July results and 489 to the May. EPA performance recommendations are MNB within ±15% and MNE<35%, both of which are met.

Day	MNB (%)	MNE (%)	N
July			
11	-2	21	5743
12	-4	21	6221
13	-5	19	6722
14	-6	21	6732
15	-3	24	6366
16	11	27	5313
17	13	24	4307
18	11	19	4679
19	-1	17	5012
average	1.6	21.4	5677
May			
24	-6	16	5817
25	-3	18	2624
26	6	21	2863
27	8	19	3683
28	4	12	2226
29	10	15	2418
average	3.2	16.8	3272

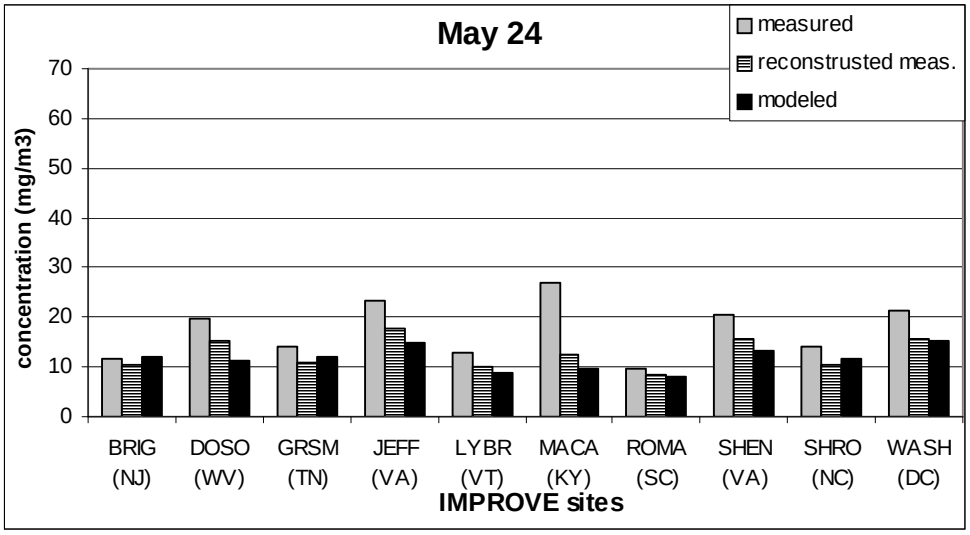
Table A.2. Mean Fractional Bias and Mean Fractional Error of $PM_{2.5}$ and sulfate predictions (%). 11 sites were available for July calculations, and 10 sites were available for May calculations.

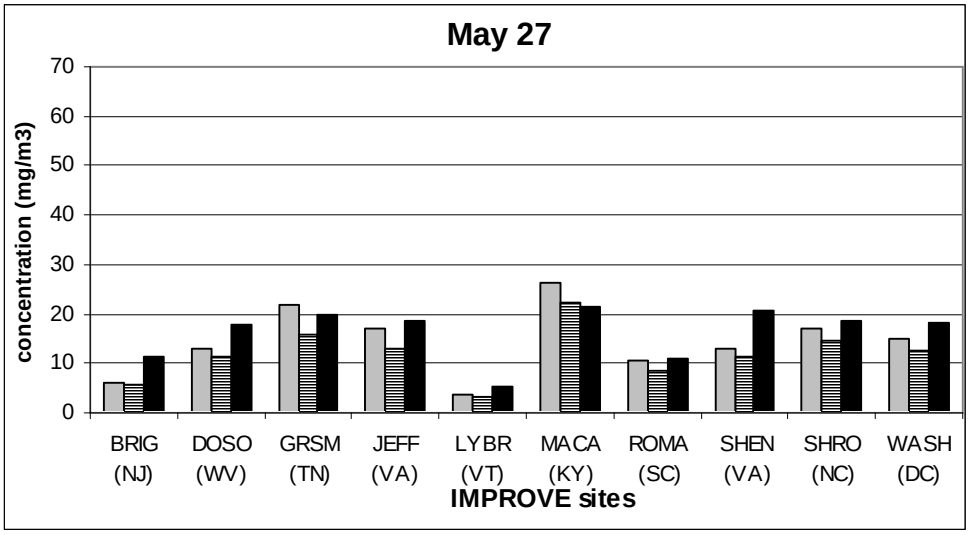
	$PM_{2.5}$		**recon** $PM_{2.5}$		**Sulfate**		**Organic Carbon**	
	MFB (%)	**MFE (%)**	**MFB (%)**	**MFE (%)**	**MFB (%)**	**MFE (%)**	**MFB (%)**	**MFE (%)**
12-Jul	-29	31	8.2	26	7.2	23	1.0	42
15-Jul	-43	59	-15	49	-11	56	-13	37
19-Jul	-14	26	11	24	-13	53	34	38
24-May	-35	36	-7.3	15	-18	26	23	41
27-May	19	24	36	37	39	41	33	39
All Days	-21	35	6.4	30	0.43	40	15	40



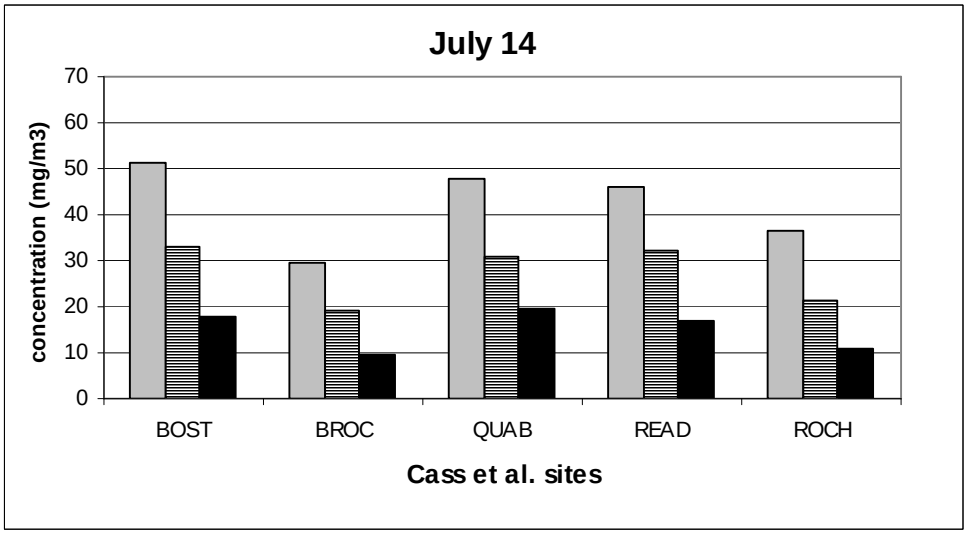
(a)

Figure A.1. Measured, reconstructed, and modeled $PM_{2.5}$ concentrations in (a) July and (b) May from the IMPROVE sites and (c) on July 14 from the Cass sites.



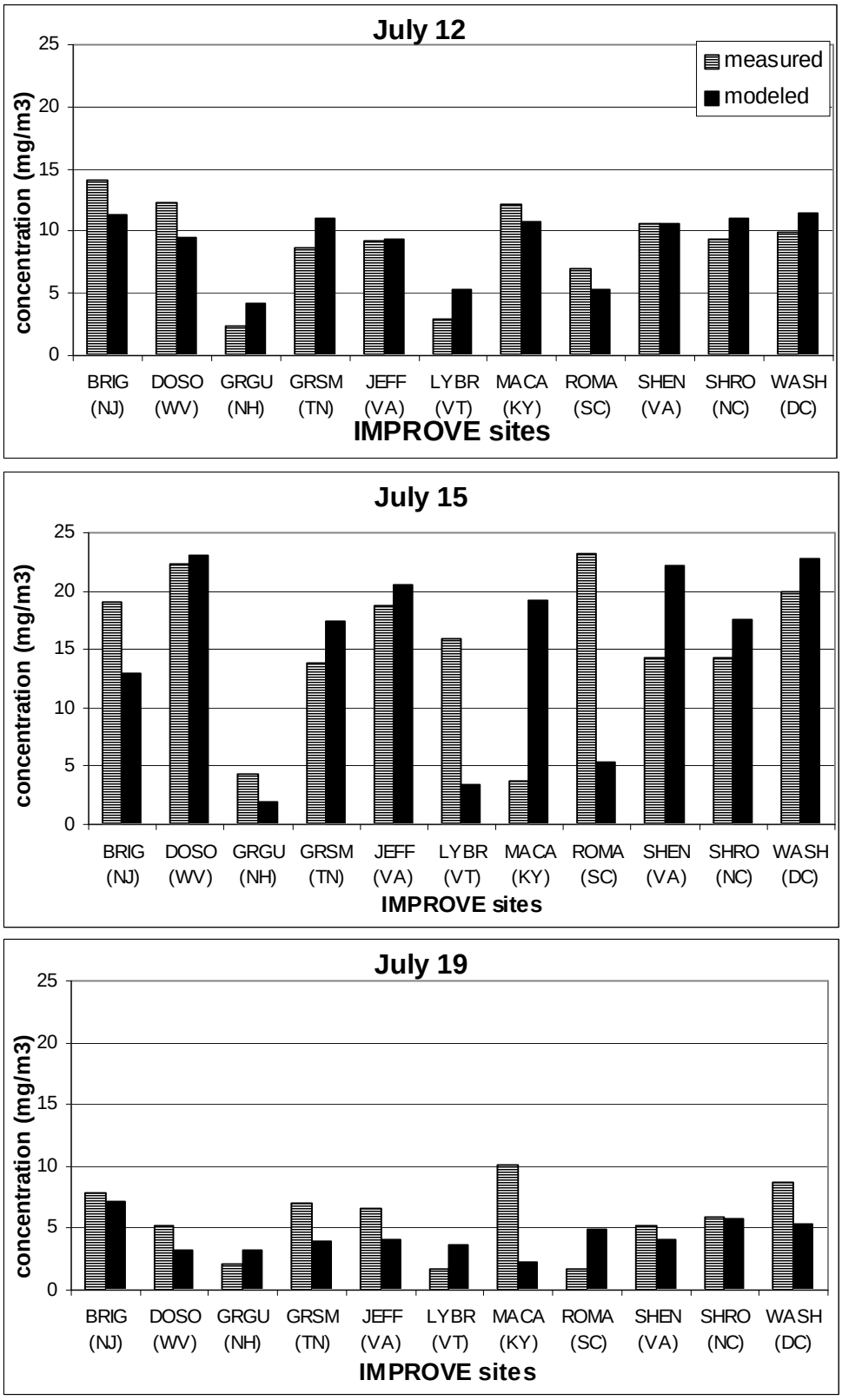


(b)



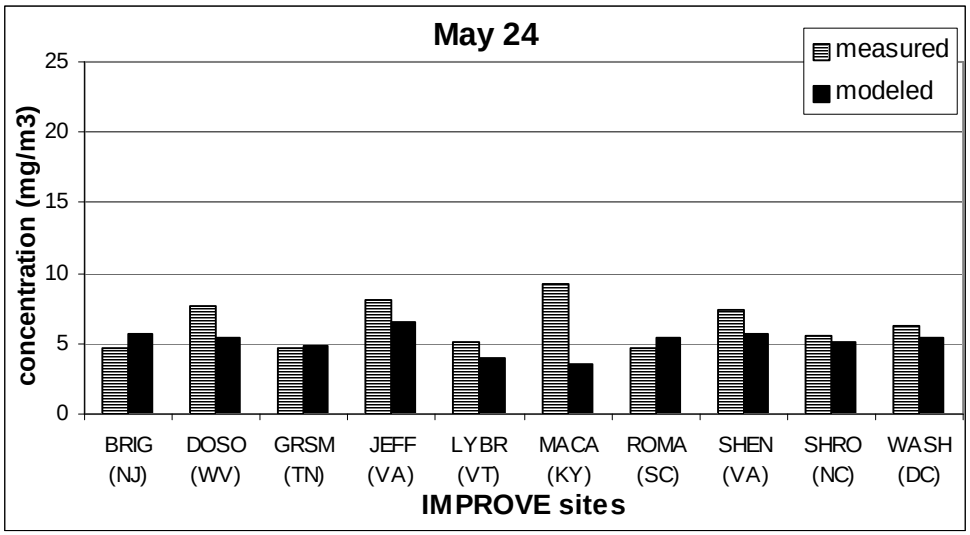
(c)

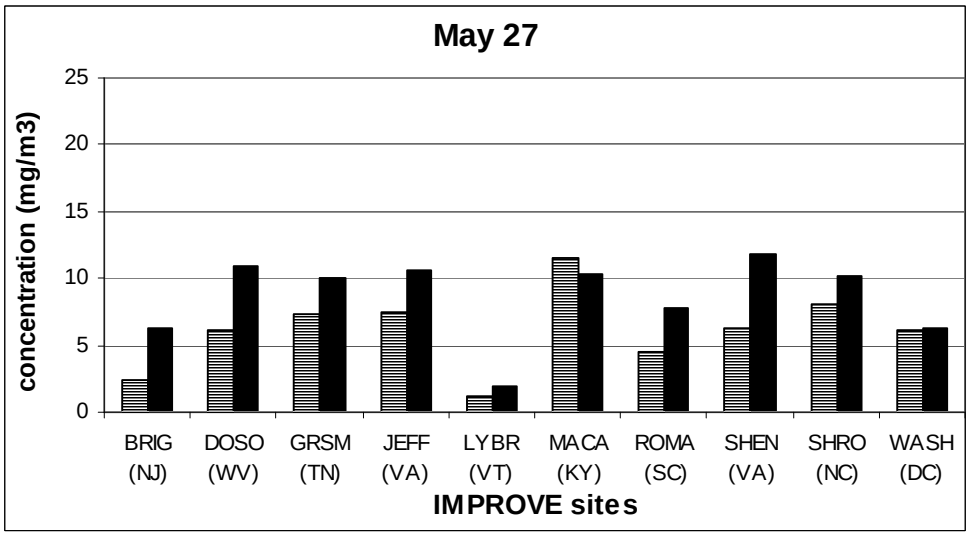
Figure A.1. Continued.



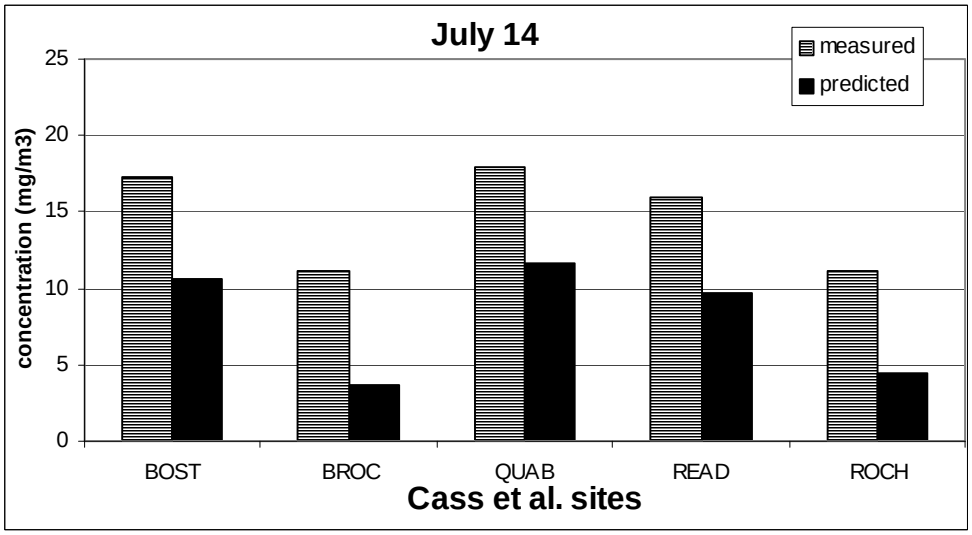
(a)

Figure A.2. Measured and modeled sulfate concentrations in (a) July and (b) May from the IMPROVE sites and (c) on July 14 from the Cass sites.





(b)



(c)

Figure A.2 Continued.

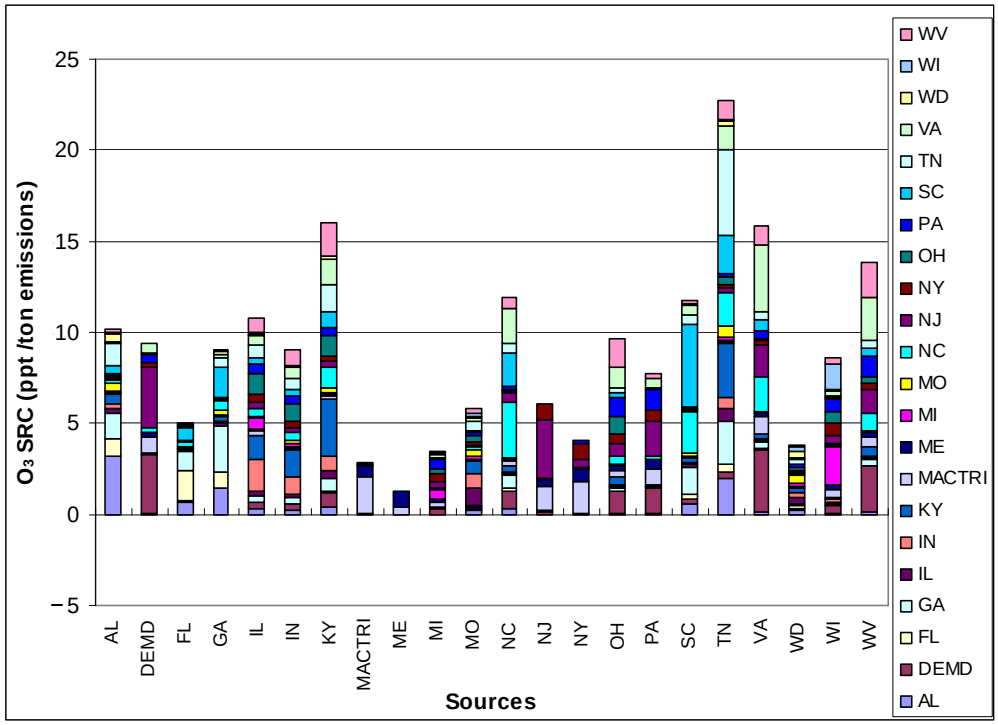
A3.Results

These results support material in the main manuscript of this paper. Please see the manuscript for a description of the calculations. In general, these supplemental figures show results for source and receptor SRCs and SRIFs. These are calculated as the sensitivity of ozone to surface NO_x and elevated NO_x during a July and May episode, and the sensitivity of $PM_{2.5}$ to SO_2, surface NOx, and elevated NO_x during a July, May, and February episode. SRCs are for a one ton emissions reduction, and SRIFs are for a 30% reduction in emissions. SRIFs are linearly combined across emission category contributions (e.g. sensitivity of ozone to a 30% reduction of elevated NO_x plus a 30% reduction of surface NO_x). For SRCs, source category contributions cannot be combined, so each emissions category is discussed separately. Because ozone is regulated on a daily maximum basis, the July and May episode results are not combined for SRCs or SRIFs. $PM_{2.5}$ is regulated on an annual average basis, so results for the three episodes are averaged.

A3.1. States as sources

(a) Ozone SRCs

(a)



(b)

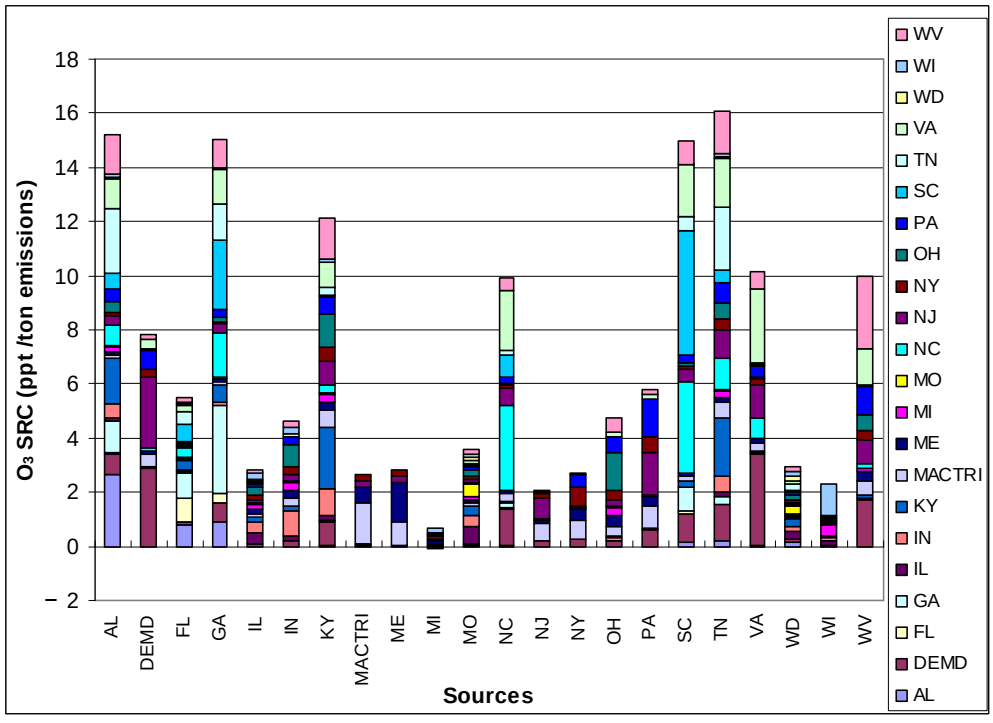


Figure A.3. Ozone Source Receptor Coefficient contributions from one ton reductions in (a) elevated NO_x emissions during the July episode and (b) surface NO_x and (c) elevated NO_x emissions during the May episode

(c)

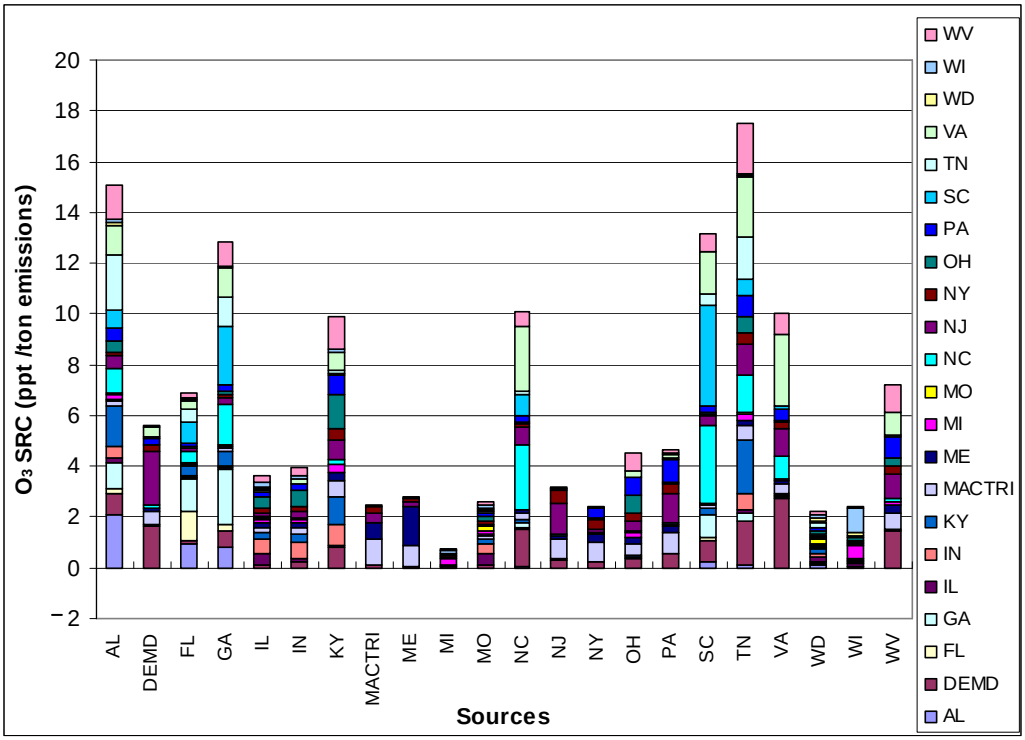
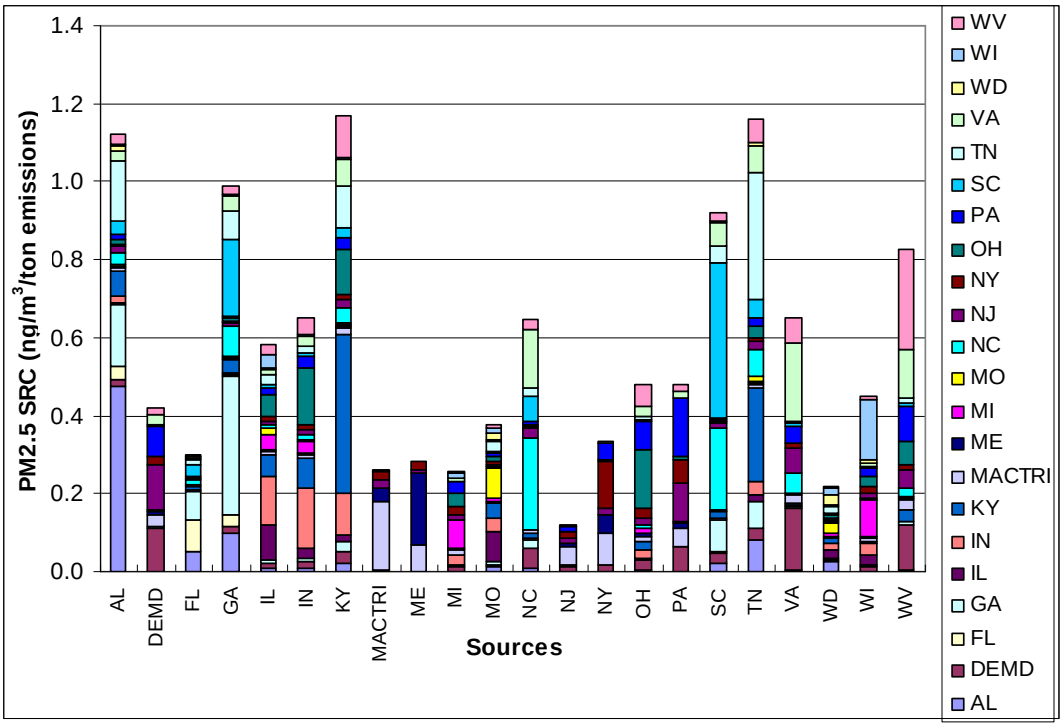
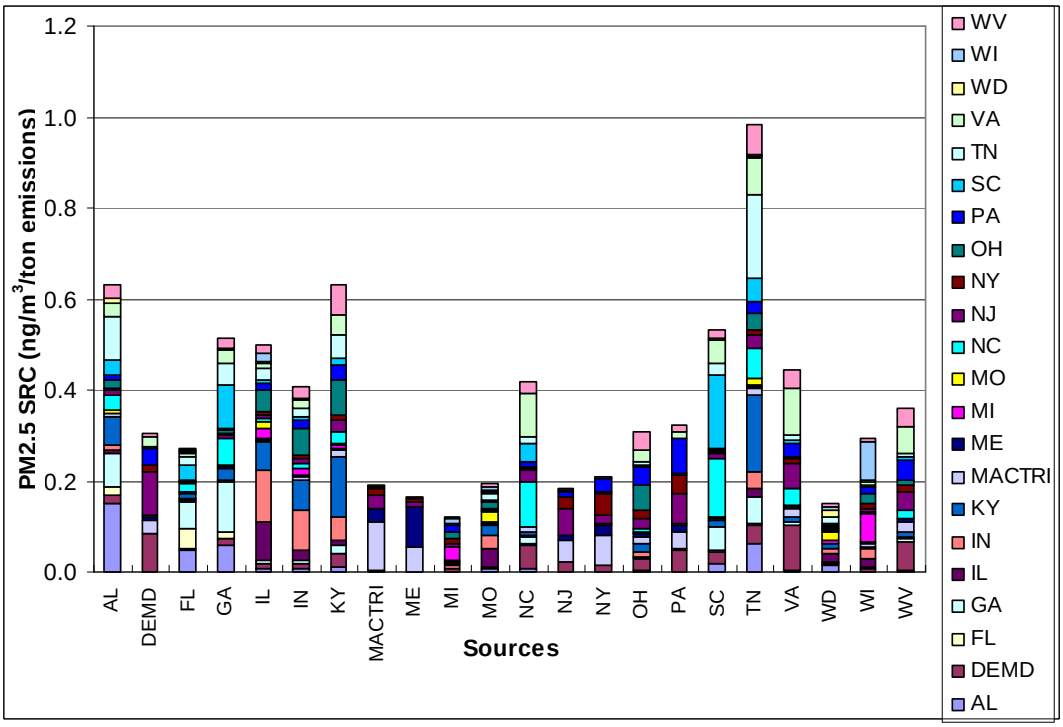


Figure A.3. Continued

A3.1(b) $PM_{2.5}$ SRCs



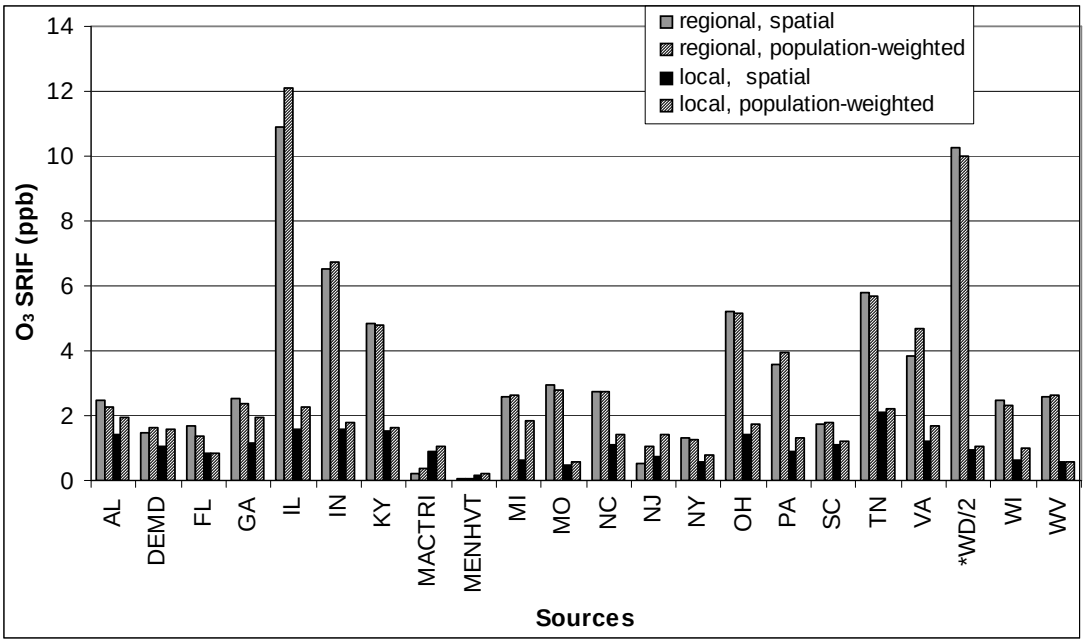
(a)



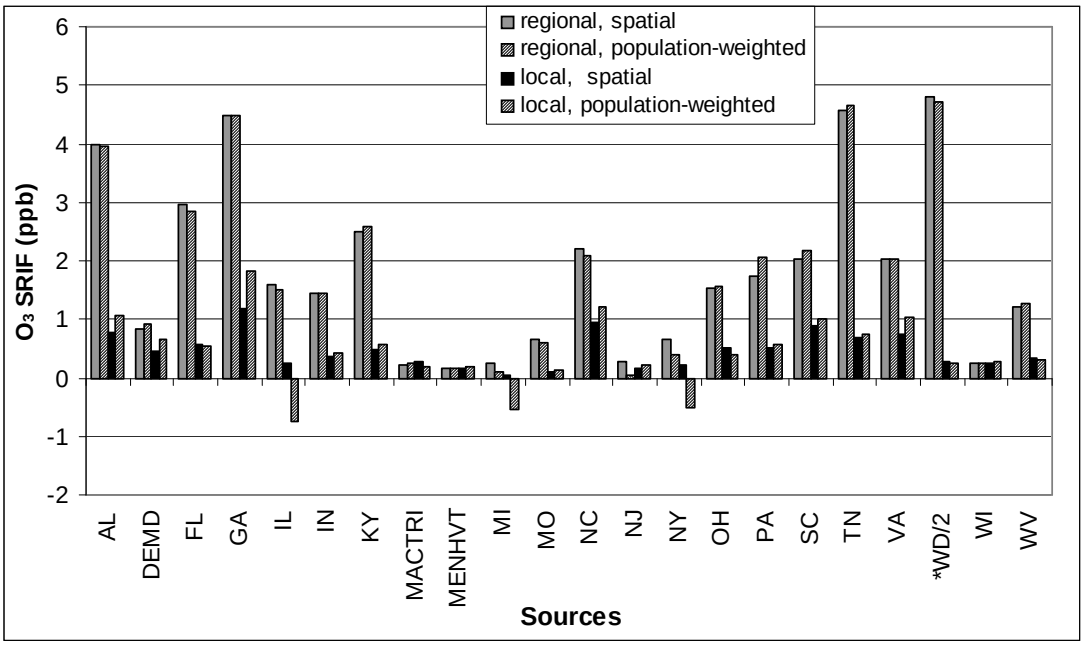
(b)

Figure A.4. $PM_{2.5}$ Source Receptor Coefficient contributions from one ton reductions of (a) surface NO_x and (b) elevated NO_x averaged over the July, May, and February episodes.

A3.1(c) Spatial and population weighted local and regional SRIFs



(a)



(b)

Figure A.5. Comparison of spatial and population-weighted Source Receptor Impact Factors contributed by each state to local and regional (a) ozone from surface and elevated NO_x emissions for the July episode and (b) the May episode, and (c) to PM25 from SO_2 and surface and elevated NO_x emissions averaged over the July, May, and February episodes.

(c)

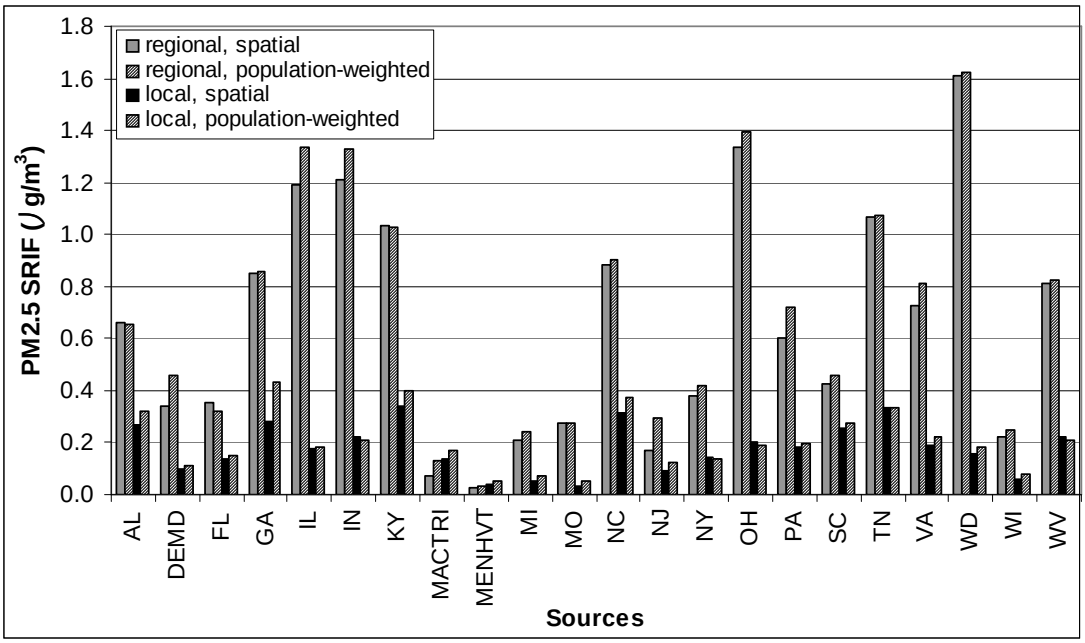


Figure A.5. Continued.

A3.2. States as receptors

A3.2(a) Ozone spatial and population weighted SRIFs, May episode

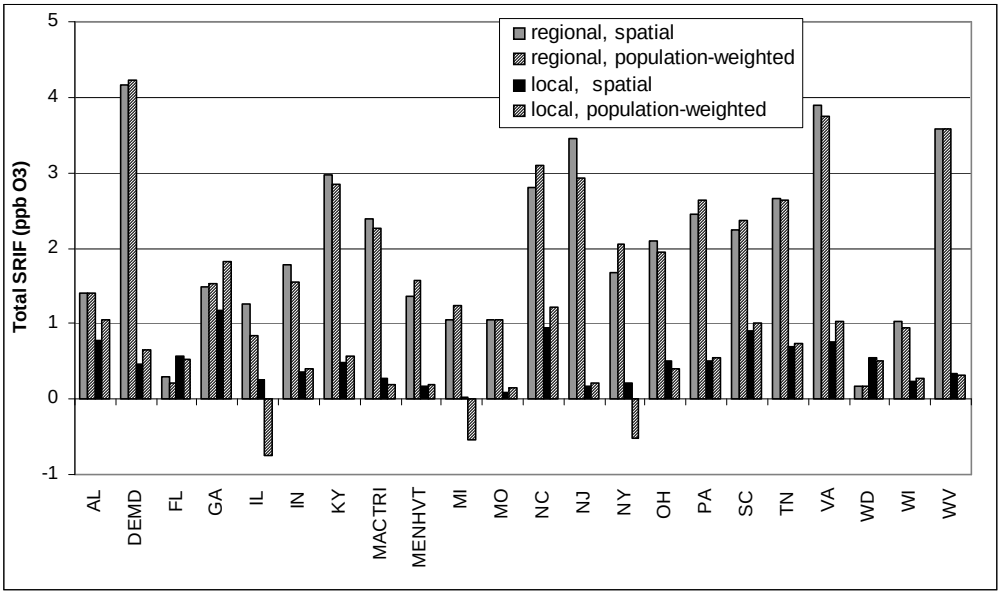
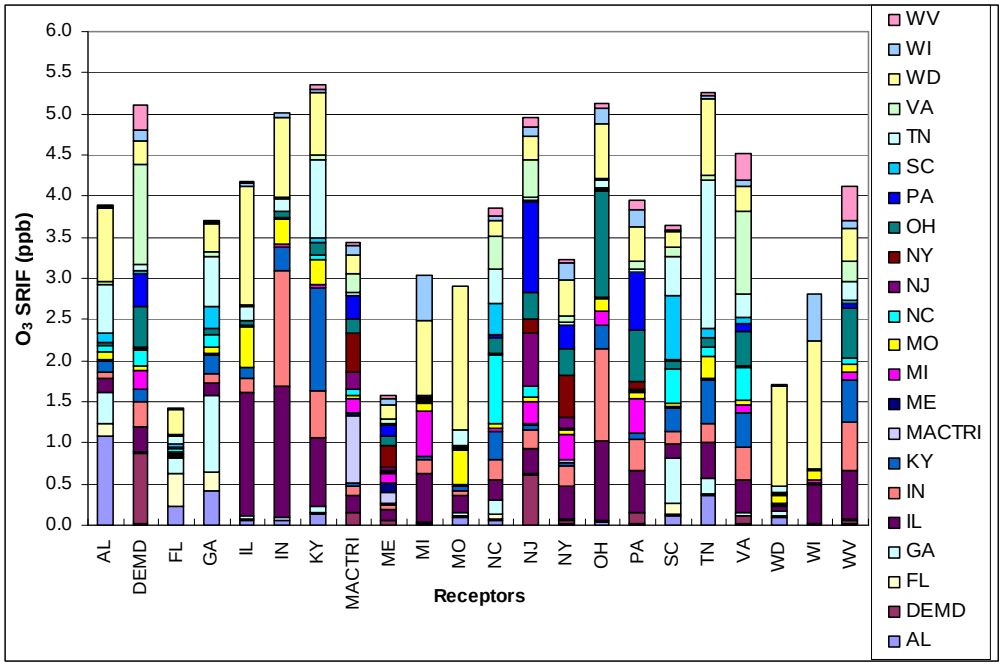
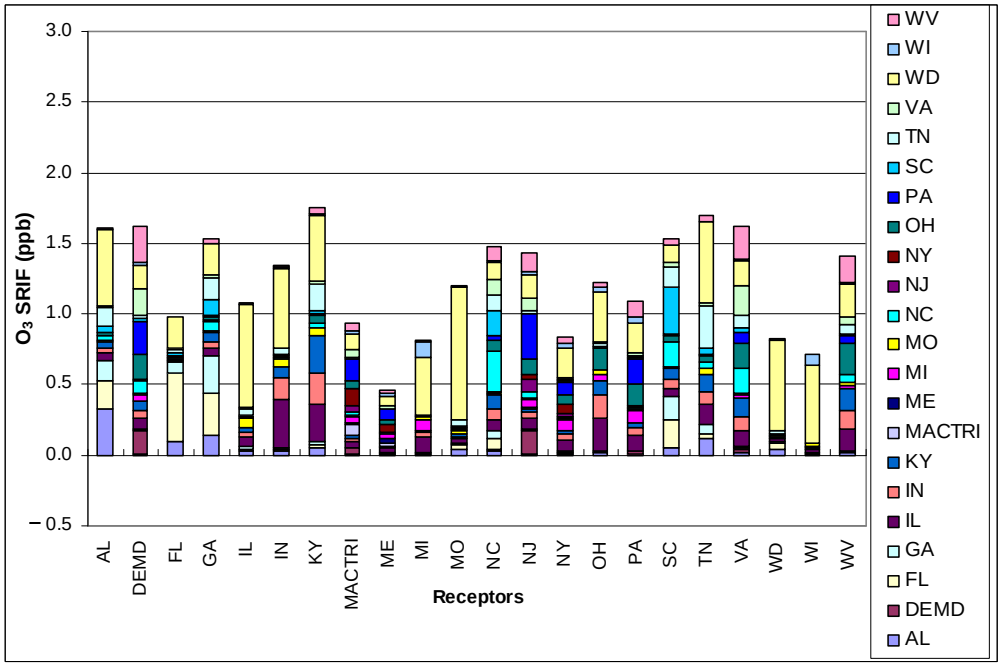


Figure A.6. Comparison of spatial and population-weighted Source Receptor Impact Factors on ozone in each receptor state from local and regional surface and elevated NO_x emissions for the May episode.

A3.2(b) Ozone SRIF receptors



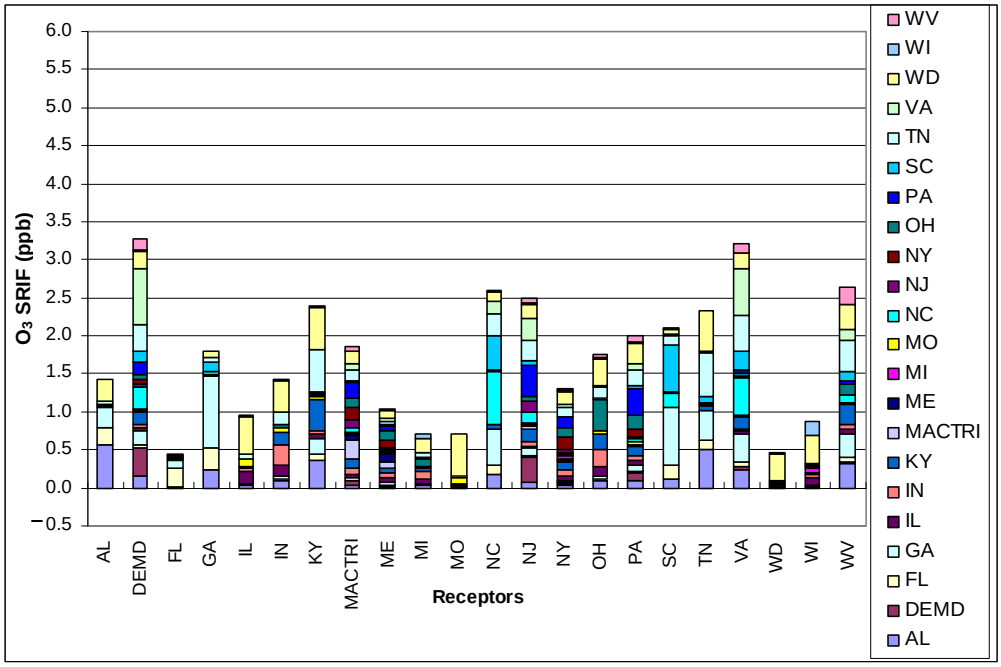
(a)



(b)

Figure A.7. Source Receptor Impact Factors in each state for ozone sensitivity to 30% reductions in (a) surface NO_x and (b) to elevated NO_x emissions during the July episode, and (c) to surface NO_x and (d) to elevated NO_x emissions during the May episode.

(c)



(d)

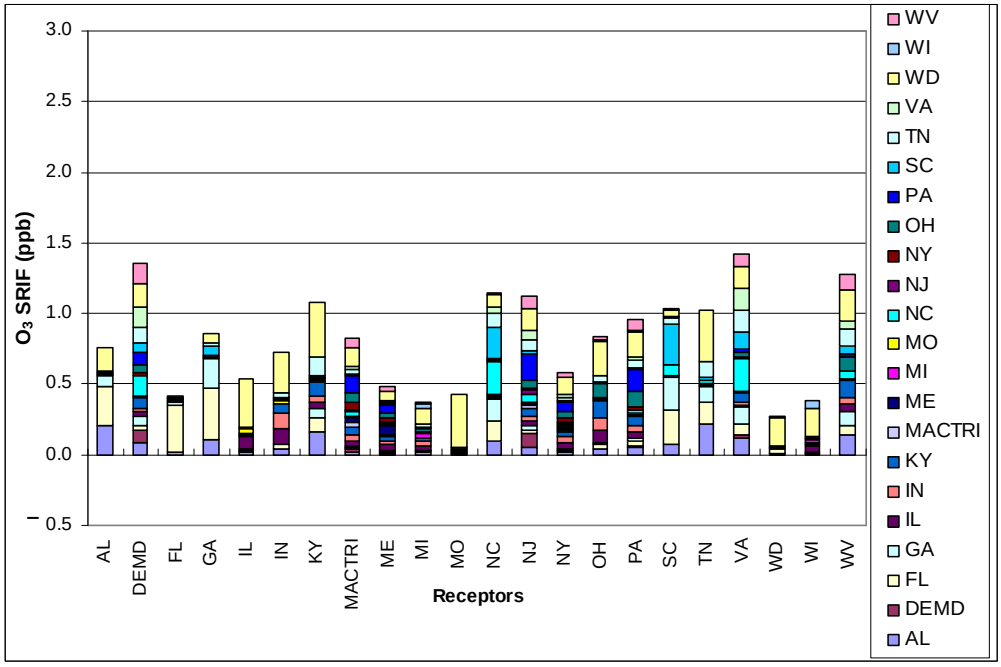
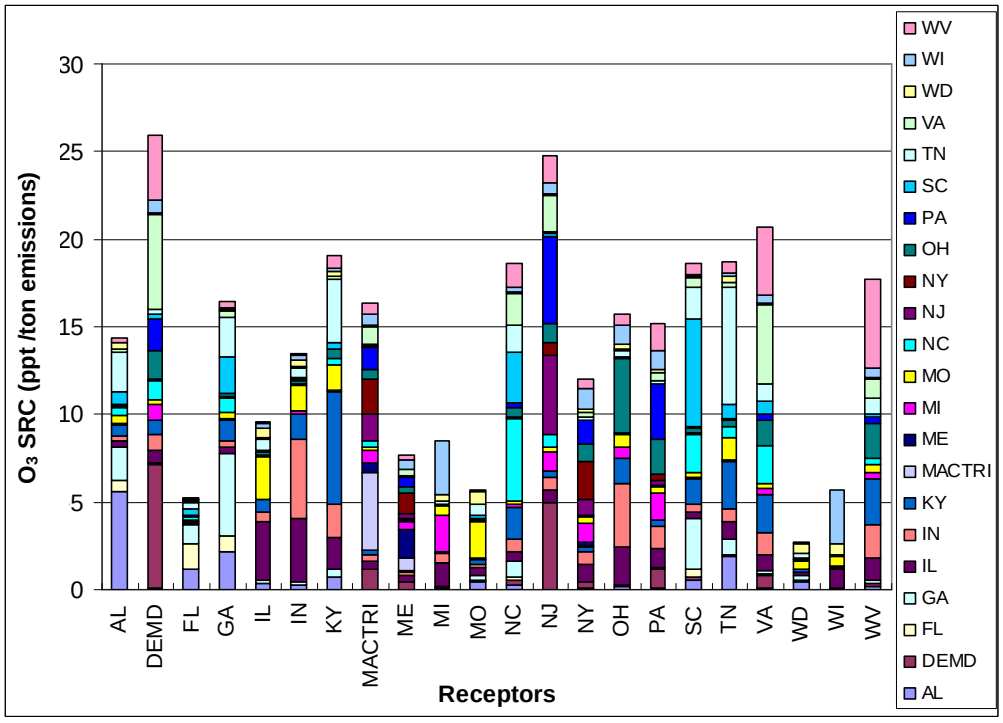


Figure A.7. Continued.

A3.2(c) Ozone SRC receptors

A few states show ozone increases in response to NO_x reductions (i.e. negative SRCs), particularly when weighting sensitivities by population and during the May episode. In particular, NY, MI, and IL all have low local negative population-weighted SRCs in response to surface NO_x reduction in May (-1.48, -1.79, and -1.88 ppb respectively). NY also has a negative local SRC of -2.1 ppb in May in response to elevated NO_x reductions. The May episode is more VOC-limited than the July episode, so NO_x is titrating ozone in areas with high ozone concentrations. In July, elevated NO_x reductions in New Jersey lead to a fairly large increase in population-weighted ozone in Pennsylvania (-1.58 ppb), the results for which are dominated by the city of Philadelphia.

(a)



(b)

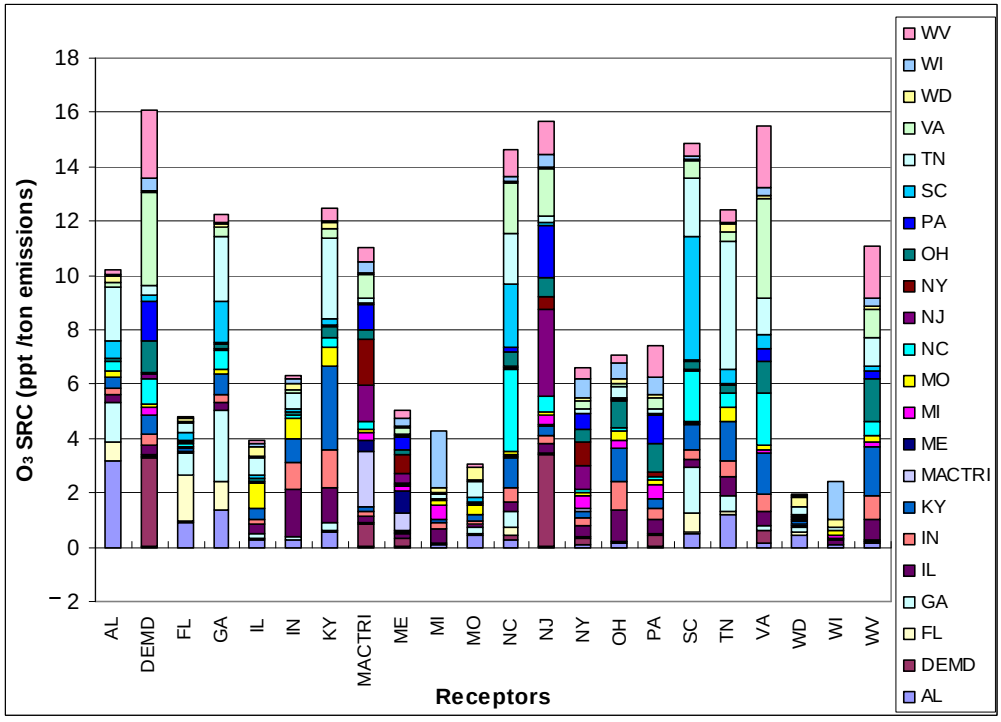
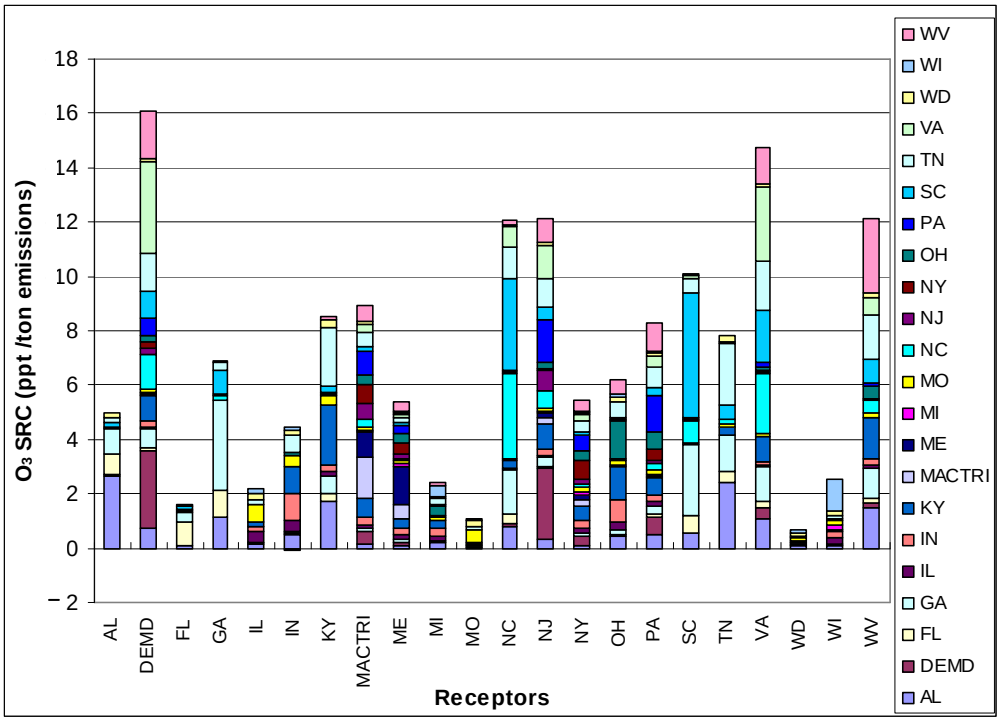


Figure A.8. Ozone Source Receptor Coefficients in receptor states from one ton reductions in (a) surface NO_x and (b) from elevated NO_x emissions during the July episode, and (c) from surface NO_x and (d) from elevated NO_x emissions during the May episode.

(c)



(d)

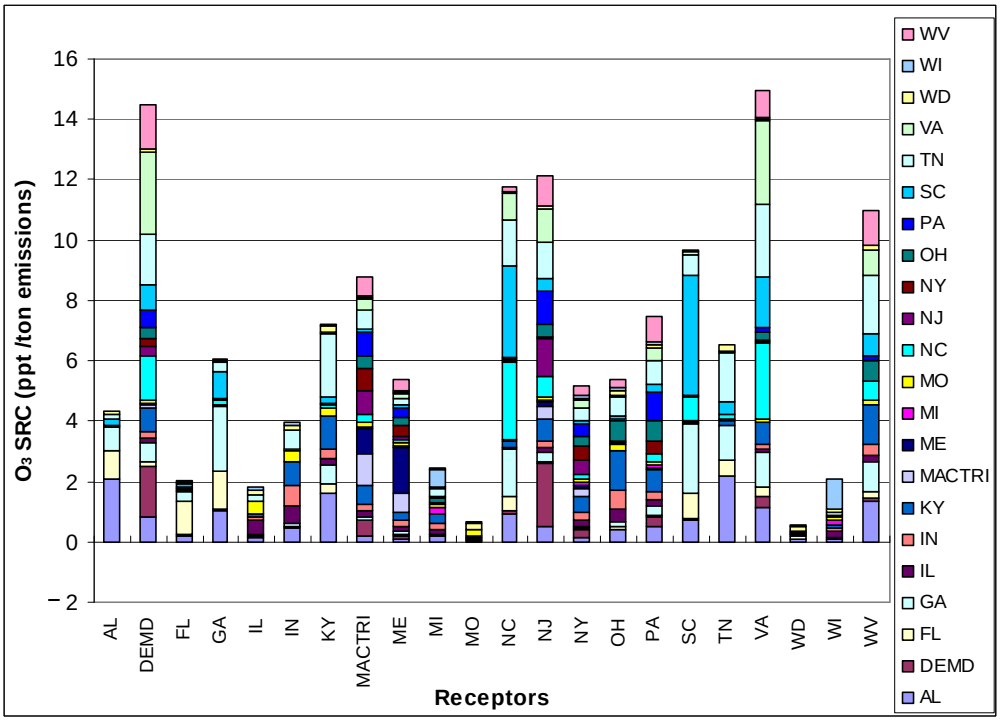
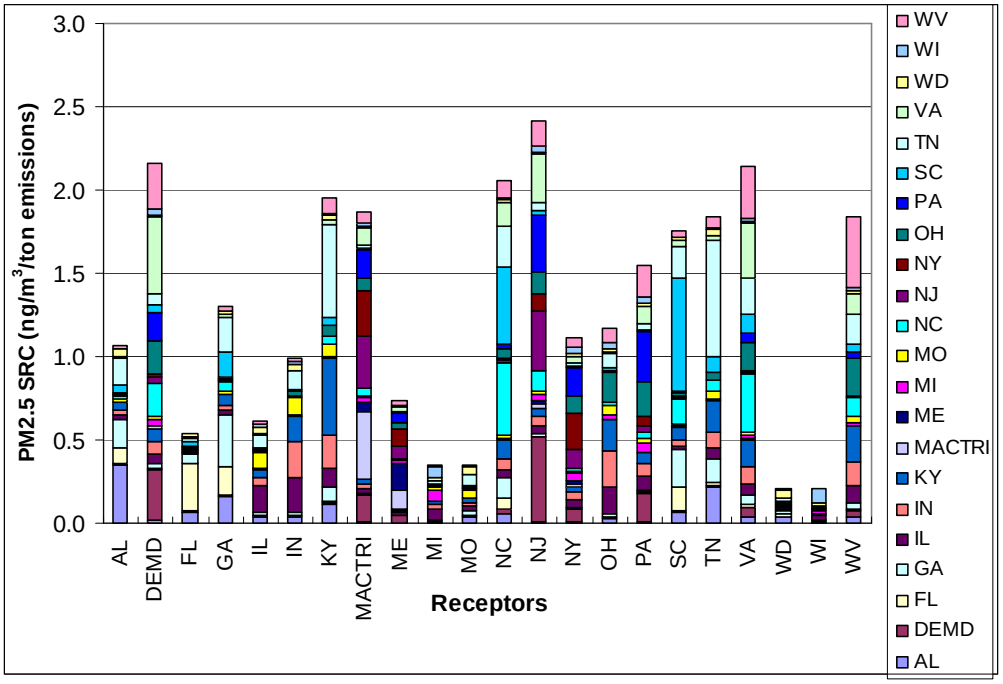


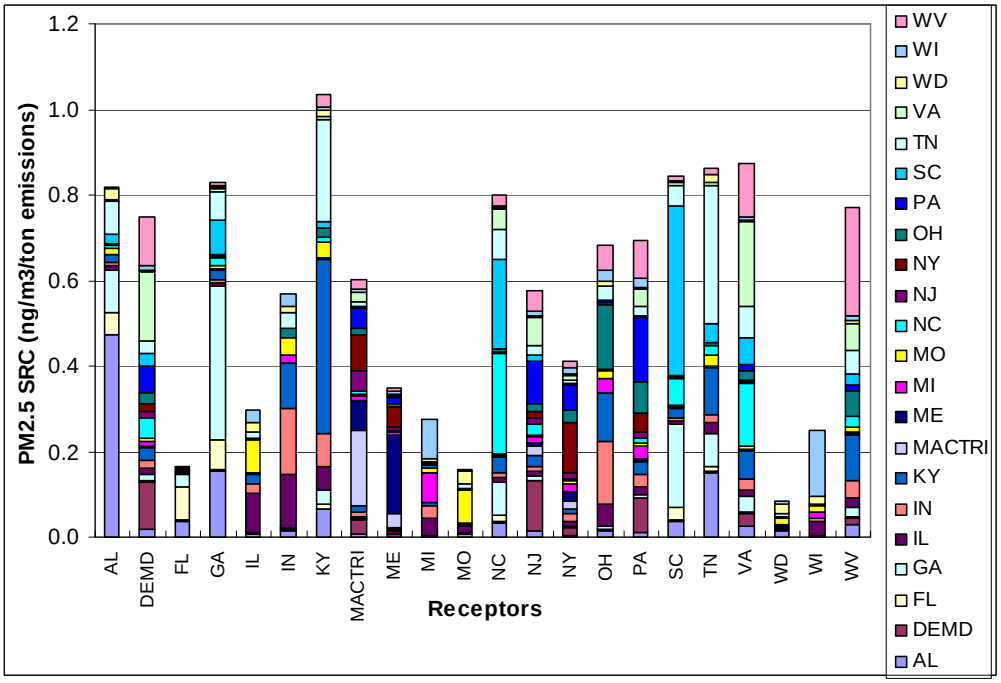
Figure A.8. Continued.

A3.2(d) $PM_{2.5}$ SRC receptors

Almost all individual $PM_{2.5}$ SRCs are positive, and those that are negative are generally quite low and occur only to NO_x emission reductions.



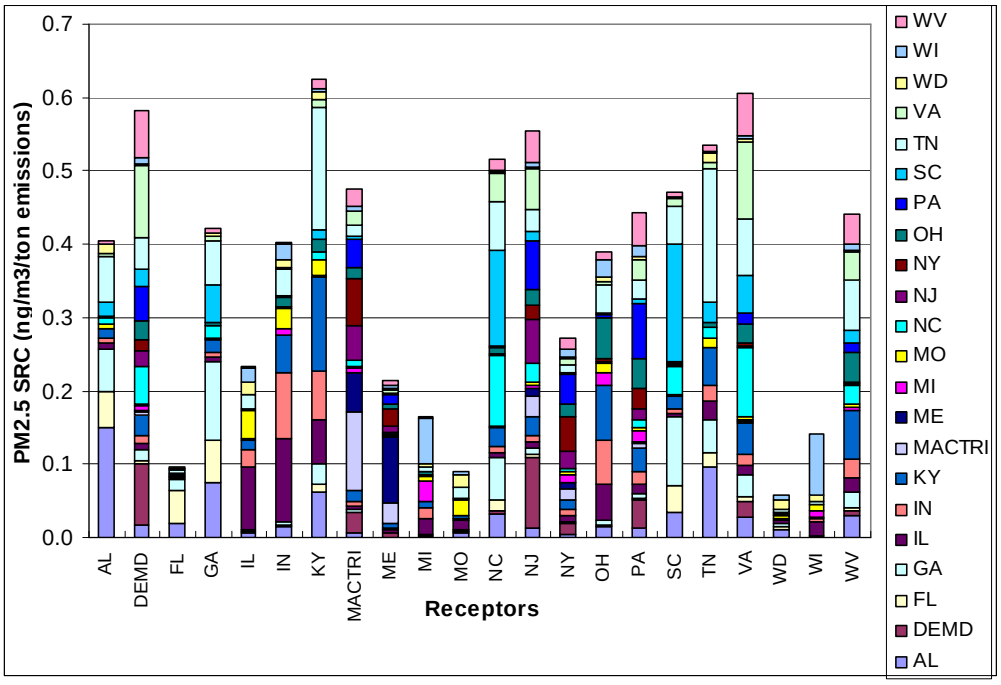
(a)



(b)

FigureA9. $PM_{2.5}$ Source Receptor Coefficients in receptor states from one ton reductions of (a) SO_2, (b) surface NO_x, and (c) elevated NO_x emissions averaged over the July, May, and February episodes.

(c)



FigureA9. Continued.

REFERENCES

Andrews, E., P. Saxena, S. Musarra, L. M. Hildemann, P. Koutrakis, P. H. McMurry, I. Olmez and W. H. White (2000). "Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements." *Journal Of The Air & Waste Management Association* **50**(5): 648-664.

Berkowitz, C., R. Easter and S. BC (1989). "Theory and results from a quasi-steady-state precipitation-scavenging model." *Atmospheric Environment* **23**(7): 555-1571.

Boylan, J. W., M. T. Odman, J. G. Wilkinson and A. G. Russell (2006). "Integrated Assessment Modeling of Atmospheric Pollutants in the Southern Appalachian Mountains. Part II: Fine Particulate Matter and Visibility." *J. Air & Waste Manage. Assoc.* **56**: 121-122.

Boylan, J. W. and A. G. Russell (2006). "PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models." *Atmospheric Environment* **40**(26): 4946-4959.

EPA (1991). Guidance for Regulatory Application of the Urban Airshed Model (UAM). . Research Triangle Park, NC.

EPA (1994). US Environmental Protection Agency, Office of Air and Radiation, Office of Mobile Sources, Emissions Planning and Strategies Division, Air Quality Analysis Branch. User's Guide to MOBILE5 (Mobile Source Emission Factor Model). EPA-AA-TEB-94-01. Ann Arbor, MI.

EPA (2001). US Environmental Protection Agency, Office of Air Quality Planning & Standards, Information Transfer & Program Integration Divsion, Information Transfer Group. EPA AIRS Data. Available from: http://www.epa.gov/airsdata

Nenes, A., S. N. Pandis and C. Pilinis (1998). "ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols." *Aquatic Geochemistry* **4**(1): 123-152.

NPS (1995). University of CA, Davis, for the National Park Service, Air Quality Research Division. IMPROVE Data Guide: A Guide to Interpret Data. Fort

Collins, CO. Available from: http://vista.cira.colostate.edu/improve/Data/IMPROVE/improve_data.htm

Odman, M. T., J.W. Boylan, J.G. Wilkinson, A.G. Russell, S.F. Mueller, R.E. Imhoff, K.G. Doty, W.B. Norris, R.T. McNider (2002). "Integrated modeling for air quality assessment: The Southern Appalachians Mountains initiative project." *J. Phys. IV France* **12**: 211-234.

Odman, M. T. and A. G. Russell (1991). "Multiscale Modeling of Pollutant Transport and Chemistry." *Journal of Geophysical Research-Atmospheres* **96**(D4): 7363-7370.

Pandis, S. N., R. A. Harley, G. R. Cass and J. H. Seinfeld (1992). "Secondary Organic Aerosol Formation and Transport." *Atmospheric Environment Part a-General Topics* **26**(13): 2269-2282.

Pandis, S. N., A. S. Wexler and J. H. Seinfeld (1993). "Secondary Organic Aerosol Formation and Transport .2. Predicting the Ambient Secondary Organic Aerosol-Size Distribution." *Atmospheric Environment Part a-General Topics* **27**(15): 2403-2416.

Pechan (2001). Pechan/Avanti Group. Southern Appalachian Mountains Initiative (SAMI) emissions projections to 2010 and 2040: growth and control data and emission estimation methodologies.

Pielke, R. A., W. R. Cotton, R. L. Walko, C. J. Tremback, W. A. Lyons, L. D. Grasso, M. E. Nicholls, M. D. Moran, D. A. Wesley and a. Lee et (1992). "A comprehensive meteorological modeling system-RAMS." *Meteorology and Atmospheric Physics* **49**(1-4): 69-91.

Pierce, T. E. (1996a). "Documentation for BEIS2". ftp://monsoon.rtpnc.epa.gov/pub/beis2/SOS/AAREADME.

Pierce, T. E., Geron, C.D. (1996b). "The personal computer version of the biogenic emissions inventory system (PCBEIS2.2). AAREADME". anonymous ftp at monsoon.rtpnc.epa.gov located in/pub/beis2/pcbeis22.

Pierce, T. E., Lamb, B.K., Van Meter, A.R. (1990). Development of a biogenic emissions inventory system for regional scale air pollution models. 83rd Annual Meeting of the Air and Waste Management Association, Pittsburgh, PA.

Salmon, L. G., Cass, G.R., Pedersen, D.U., Durant, J.I., Bigg, R., Lunts, A., Utell, M. (1999). Determination of Fine Particle and Coarse Particle Concentratrations and Chemical Composition in the Northeastern United States, 1995. Available from: http://www.nescaum.org/pdf/Cass-99nescaum-pm-composition.pdf

Scott, B. (1987). Pacific Northwest Laboratory. User's Manual for the Convective Cloud Module Version 1.0. PNL-6188. Richland, WA.

Turpin, B. J. and H.-J. Lim (2001). "Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass." *Aerosol Sci. Technol.* **35**: 602-610.

Wilkinson, J. G. (2006). Personal communication.

Wilkinson, J. G., C. F. Loomis, D. E. McNally, R. A. Emigh and T. W. Tesche (1994). Alpine Geophysics. Technical Formulation Document: SARMAP/LMOS Emissions Modeling System (EMS-95). AG-90/TS26 & AG-90/TS27. Pittsburgh, PA.

Appendix B.

REACTIVITY ASSESSMENTS

A Report to the Relative Reactivity Working Group
5/5/99

M. Bergin[1], W.P.L. Carter[2], J. Milford[1], Philip J. Ostrowski[4] and A.G. Russell[1]

1 Georgia Institute of Technology, Atlanta, Ga
2 University of California, Riverside
3 University of Colorado, Boulder
4 Occidental Chemical Co.

CONTENTS

QUANTIFICATION OF VOC REACTIVITY 1
Modeling-based Assessments of VOC Reactivity 4
Trajectory Model Reactivity Assessments 5
Eulerian Model Reactivity Assessments 7
VARIABILITY IN REACTIVITY SCALES 10
CHEMICAL MECHANISM UNCERTAINTY 14
REFERENCES 17
TABLES 22
FIGURES 29

NOTES:
Much of the text on Quantification of VOC Reactivity and Variability in Reactivity Scales is from Bergin et al. (1998).

Authors names are in alphabetical order.

QUANTIFICATION OF VOC REACTIVITY

A number of possible methods to quantify the impact of a VOC on ozone formation have been examined. Early reactivity experiments were based on amounts of ozone formed when the VOC is irradiated in the presence of NO_x in environmental chambers (e.g., Wilson and Doyle, 1970; Altshuller and Bufalini, 1982; Laity et al, 1973). However, individual VOCs are not emitted in the absence of other reactive organics, so such experiments cannot be expected to represent atmospheric conditions. Furthermore, there are chamber wall and background effects which affect the results of such experiments, particularly if the compound reacts slowly or has radical sinks in its mechanism (Carter and Lurmann, 1990, 1991; Carter et al, 1982; Bufalini et al, 1977; Joshi et al, 1973; Jeffries and Sexton, 1993). An alternative measure that has been proposed is comparison of the OH radical rate constants between VOCs (e.g., Darnall et al, 1976; CARB, 1989; Chameides et al, 1992). The EPA has for the most part has used the OH rate constant (with ethane as the boundary) for exempting compounds from VOC regulations (Dimitriades, 1996). Although not strictly a measure of ozone formation, for most compounds reaction with OH is the main process that initiates the VOC's ozone-forming reactions. This approach has the significant advantage that the OH rate constants are known or can be estimated for essentially all VOCs of relevance to most regulatory applications (Atkinson, 1987, 1989, 1990, 1994), and the OH rate constants are properties only of the VOC, and not the environment where the VOC is emitted (other than small temperature dependencies.) However, a significant number of compounds also react nonnegligibly with ozone, NO_3 radicals or by direct photolysis, and also this method does not account for the significant differences in the subsequent reaction pathways of the initial products, which can affect how much ozone is formed after the VOC-OH reaction OH (Carter and Atkinson, 1989; Carter, 1994).

In particular, model calculations have shown that incremental reactivities of VOCs depend not only on how fast the VOC reacts, but also on the tendency of the VOC to enhance or inhibit radical levels, the tendency of the VOC to remove NO_x from the system, and the reactivity of the VOC's major products (Atkinson, 1990; Carter and Atkinson, 1989; Bowman and Seinfeld, 1994a, 1995). For example, aromatics, which have strong NO_x sinks and radical sources in their mechanisms, are predicted to have relatively high reactivities under low VOC/NO_x conditions, but are predicted to have negative reactivities when the VOC/NO_x ratio was sufficiently high. For this reason, the OH radical rate constant has been shown to correlate poorly with other measures of ozone formation potential, particularly for the more rapidly reacting VOCs (e.g., Dodge, 1994, Carter, 1991).

Because of the limitations of the OH radical rate constant scale, Weir et al. (1988), and Carter (1991) argued that a scale based on *incremental reactivities* would provide a more comprehensive measure of the effect of a VOC on actual ozone formation. This is defined as the change in ozone caused by a change in the emissions of a VOC in a specific air pollution episode. To remove the dependence on the amount of VOC added, incremental reactivity is defined by Equation B1 as the limit as the amount of VOC added approaches zero, i.e., as the *derivative* of ozone with respect to VOC (as shown on the lower plots of Figure B1):

$$IR_i = \frac{\partial[O_3]}{\partial[VOC_i]} \qquad \text{(B1)}$$

Here, IR_i is the incremental reactivity and the subscript i denotes the VOC being examined. This reactivity definition takes into account the effects of all aspects of the organic's reaction mechanism and the effects of the environment where the VOC is

emitted. However, model calculations (Dodge, 1977; Carter, 1991, 1994; Chang and Rudy, 1990) and environmental chamber experiments (Carter et al, 1995a) have shown that changes in environmental conditions can significantly affect incremental reactivities, both in a relative and in an absolute sense. Therefore, the incremental reactivity is a function of the episode as well as the VOC. This presents obvious problems in developing reactivity scales for use in VOC control regulations that will be applicable under all conditions. Methods for dealing with this episode dependence are discussed in the section on variability below.

The incremental reactivity of a VOC under true ambient conditions cannot be measured directly— other than by changing emissions and then observing the resulting changes of air quality for enough years to factor out effects of meteorological variability— but can be estimated either by computer model calculations or by suitably designed environmental chamber experiments. Both types of estimation approaches have their limitations. In the case of model calculations, uncertainties and approximations in the model for airshed conditions, in the model formulation, and in the chemical mechanism cause uncertainties in the predicted ozone impacts, as discussed further below. In the case of experiments, it is difficult for the conditions of the experiment to simulate ambient conditions, so the results do not have general applicability. For these reasons, modeling and experimental measurements are used in conjunction for examining reactivity.

In an early model simulation, Dodge (1984) showed that, when adding a given amount of a VOC to the other VOC inputs in EKMA model simulations, the calculated change in ozone varied widely among different VOCs at low VOC/NO_x ratios, but were lower and less variable under high VOC/NO_x conditions. Carter and Atkinson (1989) showed that while the VOC/NO_x ratio was probably the most important single environmental factor affecting reactivity, other factors are important as well. Simulations of environmental chamber experiments resulted in different incremental reactivities (both

absolute and relative) than simulations of atmospheric conditions, indicating that incremental reactivities measured in chamber experiments should not be used to assess atmospheric reactivities without the benefit of model calculations to account for the differences between chamber and airshed conditions. In addition, Carter and Atkinson (1989) showed that the number of days in the pollution episode and the nature of the other VOCs present also had a non-negligible effect on VOC reactivities. Carter (1994) showed that there was still some variability in relative reactivities among different one-day airshed model scenarios even after NO_x inputs in the scenarios were adjusted to yield consistent conditions of NO_x availability.

Jeffries and Crouse (1991) and Bowman and Seinfeld (1994a,b, 1995) looked at the factors affecting reactivity from the perspective of the chemical reactions actually responsible for ozone formation. The result was that the relative contribution of VOCs to the reactions that are directly responsible for ozone could be quite different than the relative incremental reactivities of those VOCs. This is because many VOCs have high (or negative) incremental reactivities— not because of the ozone formed by their own reactions, but because their reactions affect how much ozone is formed from other VOCs. For example, if the reactions of a VOC significantly affect radical levels they will affect how much O_3 is formed from the reactions of other VOCs, and for many VOCs this indirect effect on reactivity makes a larger contribution to its incremental reactivity than the ozone formed by the VOC's direct reactions (Bowman and Seinfeld, 1994a,b, 1995). This result has also been shown from an analysis of the results of incremental reactivity experiments carried out under maximum reactivity conditions (Carter et al, 1993, 1995b).

A general scale that ranks the reactivities of VOCs would clearly aid the development of regulatory applications that take differences in VOC reactivity into account. However, because incremental reactivities depend on environmental conditions, no incremental reactivity scale will correctly predict relative ozone impacts under all conditions (even if there were no uncertainties in the models, the chemical mechanism,

and the airshed conditions.) This can be partially accounted for through the use of a relative, rather than absolute, comparison of reactivities. In other words, we do not compare the absolute amount of ozone formed per amount of VOC added, but the amount of ozone formed relative to other VOCs. This concept is applied to sources as well as compounds. For example, if one is comparing the reactivity of emissions from a gasoline-fueled vehicle to that from a compressed natural gas (CNG) vehicle, what is most important is not that the gasoline-fueled exhaust has a reactivity of 1.00 gram of ozone per gram of exhaust VOC, and CNG exhaust has a reactivity of 0.20 grams of ozone per gram exhaust VOC. These quantities are dependent on location and time. What is of greater interest is that the CNG exhaust is 5 times less reactive, so the CNG vehicle can emit about five times as much VOC in any area and still have a similar impact on ozone levels. Defining reactivity in reference to other reactivity values rather than to absolute ozone formation allows reactivity values to be more readily evaluated and compared. To calculate relative compound reactivities, we quantify the reactivity of individual VOCs as compared to a reference compound or, better, a VOC mixture (i.e., the reactivities are normalized). When these normalized compound reactivities are quantified in a relative sense, the set of reactivities is referred to as a relative reactivity scale.

While the use of a reactivity scale reduces the effect of reactivity variability, it cannot completely account for environmental effects. Nevertheless, the only practical alternative to using a general reactivity scale is regulating all compounds as if they were either reactive or unreactive, i.e., using an implicit reactivity scale where all compounds have reactivities of either 0 or 1. This method has obvious shortcomings. For these reasons, a number of reactivity scales have been developed, and are summarized in Table B.1.

Modeling-based Assessments of VOC Reactivity

Two methods are traditionally used to assess VOC reactivity: experiments using smog chambers and computationally using air quality models. Both have limitations. Smog chambers do not realistically represent the physics of pollutant transport and impact of fresh emissions, and are generally carried out at higher pollutant levels than generally occur in the atmosphere. Therefore, the conditions inside a smog chamber do not reflect those conditions found in the ambient air. Given the sensitivity of a compounds impact (and hence reactivity) to the environment, this limits the applicability of smog chamber experiments for reactivity quantification. In addition, chamber wall effects can also impair such experiments, particularly if the compound reacts slowly or has radical sinks in its mechanism (e.g., Carter and Lurmann, 1991). Models also have limitations. All models suffer from a limited knowledge in the chemistry of specific compounds, and this directly impacts one's ability to quantify the reactivity of that compound. For many compounds, the chemical mechanism is not well known. A second limitation is that other uncertainties lead to uncertainties in how a model treats the dynamics of various compounds. However, the models have been developed to accurately represent the various physical and chemical processes that impact the dynamics of trace gases in the atmosphere, so they provide a method to quantify reactivity in the atmosphere. Computational modeling has been the approach taken in most recent reactivity quantification studies (e.g., Carter and Atkinson, 1989; Carter, 1994; Derwent and Jenkins, 1991; Bowman and Seinfeld, 1995; McNair et al., 1992; Yang et al., 1995; Bergin et al., 1995).

The various types of model's used for reactivity assessments include box, trajectory and three-dimensional models (also called airshed models). The differences in these models are described in the section on modeling. The three-dimensional models have the fewest limitations in their formulation, and can also provide spatial information,

e.g., how compound reactivities change over an airshed. Thus, they are the most powerful approach. On the other hand, they are the most computationally intensive and until recently could not be used with the more detailed chemical mechanisms which are required for reactivity assessment. In addition, the input data usually have major uncertainties, and if the input data are incorrect the model predictions may be no more accurate than those using simpler models. The simpler models (e.g., box and trajectory models) permit a wider variety of scenarios and more cases to be examined, in greater chemical detail and at lower cost. Simpler models were used for the first reactivity assessments, and the more recent assessments were conducted using multidimensional models applied at urban and regional scales. Both types of models, because of their individual strengths, continue to have a role in reactivity quantification. A list of model-based reactivity assessments is given in Table B.1.

Trajectory Model Reactivity Assessments

The first set of reactivity assessments were conducted using single cell trajectory models so that a detailed chemical mechanism could be used and the model could be applied to a number of areas. Using this approach, Carter (1994) developed a total of 18 reactivity scales, all calculated using the SAPRC-90 chemical mechanism. Subsequent versions of these scales have been calculated by Carter using the updated (SAPRC-98) version of the mechanism (Carter, 1998), but the scenarios and reactivity assessment methods were not changed.

The Carter scales represent the average results from 39 modeled trajectories, each representing a single day episode in an urban area with varying, though low, VOC-to-NO_x ratios. Averaging reactivities across these trajectories accounts for some of the variability caused by environmental conditions, as discussed further below. The 18 reactivity scales were derived using nine different approaches for dealing with the

dependence of reactivity on environmental conditions and on two methods for quantifying ozone impacts. A summary of these scales is presented in Table B.2. Of those 18 scales, the *Maximum Ozone Incremental Reactivity* (MOIR) scale and the *Maximum Incremental Reactivity* (MIR) scale were found to be reasonably representative of the full set, and are discussed in more detail below. The MIR scale reflects primarily the effect of the VOC on ozone formation rates. The MOIR, Equal Benefit Incremental Reactivity (EBIR), and the base-case average ratio ozone yield scales are more sensitive to the effect of the VOC on ultimate O_3 yields in NO_x-limited conditions. Scales based on integrated O_3 are sensitive to both factors, but tend to be more similar to MIR than MOIR (see also the discussion in following sections.) Scales sensitive to effects of VOCs on ozone formation rates generally give higher relative reactivities for aromatics, and lower relative reactivities for alkanes, than those based on ultimate O_3 yields in NO_x-limited conditions.

More recently, Carter (unpublished results) calculated reactivity scales based on the effect of the VOC on maximum 8-hour average ozone levels, which is more representative of the new Federal ozone standard. The reactivities were similar to those calculated using the integrated ozone scale.

Two of the above scales that have been most seriously considered for regulatory use are the MOIR scale and the MIR scale. The MOIR is based on incremental reactivities for NO_x conditions which are most favorable to ozone formation, as indicated by the "MOR" point on the bottom-left plot in Figure B1. The MIR is based on the incremental reactivities of VOCs under relatively high NO_x conditions where the VOCs have their highest incremental reactivity, as is also shown on the bottom-left plot of Figure B1. Carter and co-workers (Weir et al, 1988; Carter, 1994) proposed using the MIR scale for regulatory applications because the MIR scale reflects reactivities under environmental conditions which are most sensitive to effects of VOC controls. The MIR scale may be less accurate than others in predicting O_3 effects under lower NO_x conditions; however, because of the lower sensitivity of O_3 under those conditions, the

practical impact of those inaccuracies is less than would be the case for the conditions where the scale is designed to apply. The MIR scale was also found to correlate well to scales based on integrated O_3 yields, even in lower NO_x scenarios. It can also be argued that this scale is appropriate when used in conjunction with a NO_x control program, which provides the most effective ozone control under low NO_x conditions.

Nevertheless, the MOIR scale is attractive because it is more representative of the "worst case" ozone formation conditions in various airsheds, and also because it tends to be more conservative in predicting substitution benefits for most alternative fuels. The MIR scale tends to predict larger reactivity benefits for slowly reacting compounds than may be appropriate, because the higher NO_x levels of MIR scenarios cause suppressed radical levels, which decrease the amount that slower reacting compounds react in the scenarios. Ultimately, CARB concluded that the MIR was a superior method to the OH scale for assessing reactivity, and used the scale as a basis for deriving Reactivity Adjustment Factors (RAFs) in California's LEV/CF regulations (CARB, 1991). RAFs are discussed further below. The MIR scale is now also widely used as a means for comparing reactivities of vehicle emissions during various driving cycles as well as with the use of alternative fuels (e.g., AQIRP, 1993).

An alternative approach that may have the best features of both the MIR and MOIR would be to use a scale based on integrated ozone or maximum 8-hour average ozone under base-case or maximum ozone conditions. This has the advantage of the MIR scale in that it performs well in predicting reactivity effects under high NO_x conditions that are most sensitive to VOCs (because it correlates reasonably well to MIR for most VOCs), while also being based on conditions of scenarios that are more representative of worst case O_3 pollution episodes. Furthermore, in the context of Eulerian model simulations where ozone impacts vary with both time and space, integrated ozone throughout the full air basin and time period of the episode is arguably a more robust measure of the exposure of the environment to ozone than the peak ozone concentration,

which might be highly localized in time and place. Comparisons of Eulerian model predictions with the MIR and MOIR scales are discussed below. An alternative series of reactivity scales derived using a trajectory model are the *Photochemical Ozone Creation Potential* (POCP) scales, also shown on Table B.1, which were calculated by Derwent and other researchers in Europe (e.g., Derwent and Jenkin, 1991; Andersson-Skold et al, 1992) using updated versions of the Derwent and Hov (1979) chemical mechanism (see Atmospheric Chemistry section) and a two-layer Lagrangian model representing various multi-day trajectories across Europe. The reactivities are calculated from the change in mid-afternoon ozone for each day in the trajectory resulting from removing the test VOC from the emissions, divided by the integrated emissions of the test VOC up to the time of the ozone observation. Different POCP scales were calculated using different trajectories, and unlike the Carter approach no scales were derived to represent multiple conditions. Most of the POCP scenarios probably represent low NO_x conditions.

A comparison of MIR, MOIR, and POCP reactivities for selected VOCs is shown on Figure B2. The MIR and MOIR scales give very similar relative reactivities for most compounds, and are consistent in predictions of which compounds are highly reactive and which are not. However, for reasons indicated above, the MOIR scale gives lower relative reactivities for aromatics, and also predicts lower relative reactivities for radical initiators such as formaldehyde, which have larger effects on rates of ozone formation than on ultimate ozone yields. The MIR, MOIR, and POCP relative reactivities generally predict similar orderings of reactivities (relative reactivities), but some significant differences are observed. The largest differences, particularly for the alkanes and methyl ethyl ketone (MEK) are probably due primarily to differences in the chemical mechanisms employed, rather than the types of scenarios employed. The mechanisms used to develop the POCP reactivities are chemically detailed and intended to be explicit, but unlike the SAPRC and Carbon Bond mechanisms have not been evaluated against chamber data, and may not adequately represent the large NO_x sink processes in the

aromatic photooxidations that give them low or negative reactivities under low NO_x conditions (see Atmospheric Chemistry section). The relatively low reactivity predictions for the higher alkanes by the SAPRC mechanisms have been verified by environmental chamber experiments (Carter and Lurmann, 1991; Carter et al, 1993, 1995b, 1997; Carter, 1995). Effects of differences and uncertainties in chemical mechanisms on reactivity scales are discussed in more detail in a later section.

Jiang et al. (1996) also used a trajectory model to evaluate reactivity. This study used the SAPRC-90 chemical mechanism in the Ozone Isopleth Plotting Research version (OZIPR) trajectory model (Gery and Crouse, 1989) to predict the reactivity of 17 VOCs and methane in the Lower Fraser Valley of Canada. This study designated nine VOCs as significant contributors to the ozone concentrations, seven which represent lumped compound groups. The greatest contributor to ozone formation was found to be ARO2, a lumped model species used to represent the xylenes and other fast reacting aromatics.

Eulerian Model Reactivity Assessment

A serious concern about the regulatory application of scales such as MIR and MOIR is that they are all based on the single cell (Lagrangian) model simulations of single-day pollution episodes. MIRs have been developed based on 10-hour simulations, whereas some organic compounds may remain in an urban airshed for 2 to 3 days, and even longer when considering regional ozone. Further, trajectory models lack the physical detail (e.g., wind shear, venting to/from the free troposphere), the spatial and temporal detail of emissions and resulting pollutants, and the multi-day pollution effects that can be represented in Eulerian models. For that reason, it is important that the scales derived using trajectory models be evaluated using more detailed models with the same chemical mechanism. Initial studies applying threedimensional air quality models to

assess reactivity have been carried out by Russell and coworkers (e.g. McNair et al, 1992; Bergin et al,1996,1998; Kahn et al, 1998a,b; Yang et al., 1998). Those studies primarily employed the Carnegie/California Institute of Technology (CIT) Model (Mc. Rae et al, 1982; Harley et al, 1993) applied to a 3-day air pollution episode in the Los Angeles air basin (Harley et al., 1994), or the Urban-to-Regional Multiscale (URM) model (Odman et al., 1994). In addition to Los Angeles-based studies, Kahn et al. (1998a) also applied the CIT model to the Swiss Plateau and Mexico City to study the use of reactivity over domains with greatly different levels of VOC and NO_x, and Kahn et al. (1998b) studied reactivity variations over a regional domain, looking at the U.S.-Mexico border region. Two of these studies (Kahn et al. 1998b and Yang et al., 1998) incorporated the Decoupled Direct Method (DDM) for computational efficiency.

A challenge in comparing VOC reactivity using results between box and grid modeling studies is the difference between quantification measures, or metrics, that can be defined from each analysis method. Differences in the spatial and temporal representation of emissions can also make the comparison of results difficult. In the Eulerian reactivity studies, incremental emissions of the test compound were modeled by increasing the test VOC proportionally to the spatial and temporal distribution of the base organic species emissions. The rates of all organic species emissions in each modeling cell for each hour were used to determine the rate of the test species emission in that cell. This is represented mathematically by Equation B2, where, at time t in model cell x, y, z, the perturbed emission (E_p) of test species i is calculated as the base emission of that species ($E_{i\,b}$) plus a fraction, (α), of the sum of the total base level emissions of reactive organic gases . Index j refers to each represented explicit or lumped emitted VOC. This modeling method accounts for the effect of emissions variation, transport, and multi-day reactions.

$$E^{p}_{i}(x,y,z,t) = E^{b}_{i}(x,y,z,t) + \alpha\Sigma_{j}E^{b}_{j}(x,y,z,t) \quad \text{(B2)}$$

In addition to different representation of emissions by trajectory and three-dimensional models, results from three-dimensional modeling can be described in a number of ways. Three of the most useful metrics are the difference between peak ozone concentrations predicted using the base and perturbed inventories, and population- and exposure-weighted exposure to ozone levels exceeding a threshold value. Further description of these metrics are presented elsewhere (McNair, et al. 1992, Bergin, et al., 1995). Eulerian model results can also be compared across different parts of the modeled domain, which have varying VOC to NO_x ratios because of pollutant emissions and transport, as well as variation in incident radiation caused by cloud cover (Bergin et al, 1995).

In an initial application of a three-dimensional model for reactivity analysis, McNair et al. (1992) used the CIT air quality model with a relatively highly lumped chemical mechanism, the Lurmann, Carter, Coyner (1987) mechanism (LCC), to quantify the reactivity of 11 individual and lumped VOCs. This study allowed comparison with single-cell model reactivity studies by others, and also between different metrics of ozone impact, including how the species impact the peak ozone as well as ozone exposure. The results showed that the MIR reactivities did not perform well in predicting peak ozone sensitivities for the model species, but performed reasonably well in predicting effects of model species on integrated ozone exposures over the air quality standard. The MOIR scale did not compare as well as MIR to airshed model derived results for either the impacts on peak ozone or on ozone exposures over the air quality standard. The comparisons of McNair et al. (1992) are complicated somewhat by the fact that the study utilized the LCC chemical mechanism, which does not correspond directly with SAPRC-90 mechanism species used in calculating the MIR and MOIR scales. However, agreement between the MIR scale and the McNair et al. (1992) ozone exposure

predictions is remarkably good considering the difference in the mechanisms, models, and ozone impact quantification techniques employed. It was noted in this study that much of the variability found could be ascribed to using a single species (CO in this case) for normalization, which is discussed further below.

Subsequent to the study of McNair et al. (1992), the SAPRC-90 mechanism was implemented in the CIT model (referred to as the CIT-S90) by Bergin et al. for more direct comparison with the MIR and MOIR reactivity scales (Bergin et al, 1995, 1998). Here, reactivities are normalized to a mixture of VOCs representative of exhaust emissions, as in the reactivity studies of Carter (1994) and Yang et al. (1995). Some differences were found which are believed to be due to multi-day pollutant carryover and cloud cover represented in the CIT model, which are not accounted for by box models. The CIT-S90 was also used to investigate effects of environmental variabilities and of chemical mechanism uncertainties on reactivities (discussed in the variability and uncertainty sections, respectively, below.) A more detailed comparison of the CIT-S90 study results and the MIR and MOIR are also presented below.

One other three-dimensional model study of reactivity is that of Kahn et al. (1998a,b), who conducted a reactivity study on VOC solvents having a wide range of reactivities. The SAPRC-90 chemical mechanism was used for this study, assuming rate constants of similarly reacting compounds for those solvents for which chamber studies have not been performed. The solvents studied included m-xylene (the most reactive), parachlorobenzotriflouride (PCBTF, a halogenated aromatic which is the least reactive), benzotriflouride (BTF), acetone, ethanol and isobutane. These compounds not only have a wide range of reactivities, but also represent a number of different types of VOCs. Using a box model to quantify the MIR and MOIR reactivities, as seen in Figure B3, they found reasonable agreement between the normalized MIR and MOIR reactivities, though the absolute reactivities differed by a factor of two. These results, along with others (Carter, 1994a; Bergin et al., 1995, 1997; Russell et al., 1995), suggest that normalizing

reactivity (i.e., using relative reactivities) removes much of the environmental variation, though species reactivities do vary in regions of low NO_x availability or very high VOC levels. Further, the VOC reactivity assessment for the U.S.-Mexico border region shows that it is currently possible to conduct reactivity assessments regionally, particularly when using a tool such as DDM. A further study (Yang et al., 1998) used a three-dimensional model to analyze both the uncertainties in relative reactivities and the spatial variability in the southern California area. That study is further discussed in the applicable sections, below.

The above studies deal primarily with assessing the reactivities of individual VOC species. In addition, a series of studies have looked at quantifying the reactivity of source emissions, e.g., how the reactivity of a mixture of VOCs emitted by a source might be affected by the methods employed, the location, and the metric of interest. A sampling of such studies is listed in Table B.3.

VARIABILITY IN REACTIVITY SCALES

One of the stronger debates on the use of reactivity quantification for determining the potential impact of VOCs on ozone is that the absolute amount of ozone formed from a given quantity of VOC is heavily dependent on the local ambient conditions, including the meteorology (wind speed, temperature, mixing height and humidity), pollutant transport (the residence time of emissions in an urban area), distribution of emissions sources (e.g., proportion of biogenic, mobile source, and other emissions), and background pollutant concentrations (e.g., the VOC/NO_x ratio and the absolute levels of VOCs and NO_x). This dependence on variable conditions was discussed above when presenting various reactivity scales and experimental results.

One effect of variable conditions is that, in the extreme, a compound can go from being fairly reactive under certain conditions to having a negative reactivity under others (e.g. toluene). This dependence may make the use of generalized reactivity weighting and the development of reactivity-based control strategies problematic. However, one should also recognize that for most of the organics, those that are highly reactive relative to the other VOCs under one set of conditions remain highly reactive under other conditions. Likewise, the less reactive VOCs remain less reactive. Compounds that vary widely, such as toluene, are the exception rather than the rule. As discussed above, this variation can be reduced by the use of normalizing and relative ranking in the reactivity quantification of VOCs.

For example, in 1990, CARB (1991, 1993) adopted the LEV/CF regulations, where vehicle exhaust emissions standards used "Reactivity Adjustment Factors" (RAFs), which are ratios of reactivities of the alternatively fueled to conventionally fueled exhausts, to account for the reactivity differences of these exhausts. The impact of environmental condition variability on RAFs was investigated by Russell et al. (1995), who calculated both the absolute reactivities and the RAFs of exhaust from vehicles operated on six fuels along each of the 39 trajectories used in developing the MIRs. The results are shown by box plots in Figure B4. The variation in absolute ozone forming potentials across cities is substantial. However, in the case of the RAFs, where the reactivities of the exhausts are normalized by the reactivity of standard gasoline exhaust, variation among cities is sharply diminished (Figure B4). Again, it is the relative ozone impact that is of greatest concern. Such a marked decrease may not be found for source types emitting fewer compounds.

A second issue in the analysis of variability in reactivity with environmental conditions is the effect of NO_x and VOC background concentrations. The MIR scale was derived using conditions relatively high in NO_x, as might be experienced in areas with a high density of NO_x emissions (e.g., areas highly impacted by traffic or local industries

with significant combustion sources). MOIR conditions occur at lower NO_x levels, but the ROG/NO_x ratios are still lower than what might be found in rural areas. Reactivity simulation conditions used by Derwent and co-workers (1991) have even less NO_x, which represents conditions where VOC controls and reactivity weighting are relatively ineffective (as discussed below). So the question arises as to how well a measure of reactivity quantification can represent many areas, given the possible range of environmental conditions under which ozone formation occurs. This was, in part, addressed above when comparing the MIR, MOIR, and POCP scales, and is addressed further below.

The impact of environmental conditions on reactivity should be discussed at two levels. First, how it affects the reactivity of individual VOCs; and second, how it would likely affect the reactivity of emissions from a source whose composition is made up of a large number of VOCs. As suggested above, the absolute amount of ozone formed from any VOC is highly dependent on the environmental conditions. In an area already rich in VOCs (i.e., a NO_x-limited regime), the small addition of an individual VOC has a lower impact than if that same increment of VOC emissions occurs in an area rich in NO_x (where ozone formation is VOC-limited). As shown by Carter (1994), the average absolute reactivity of a suite of VOCs using the MIR scale is about twice that when using the MOIR scale. Further, there are those few compounds that can go from having relatively high reactivities to low or negative reactivities. This would appear to inhibit the use of reactivity weighting in regulatory applications.

An interesting exercise that addresses the impact of environmental variabilities is a comparison between trajectory model results and three-dimensional model results. By their nature, the three-dimensional models cover domains with a wide range of environmental conditions, going from NO_x-rich conditions in urban centers to VOC-rich conditions downwind. Further, they can follow the transport of pollutants over long distances. In the Bergin et al. (1995, 1998) modeling studies described previously, the

spatially and temporally resolved ozone impacts were used to calculate impacts on the peak ozone, the potential population-weighted ozone exposure, and the spatial-weighted ozone exposure. From those calculations, the corresponding compound reactivities were quantified, normalized to the reactivity of a mixture of VOCs (so the results are relative reactivities.) As shown in Figure B.5, the results from the MIR and MOIR box model calculations (Carter, 1994a), conducted for 39 cities, agreed well with related metric results from the airshed calculations for the Los Angeles, California area (as described further below).

In interpreting the results of the comparison between the two modeling approaches, and the differences found between the three metrics defined for the airshed model results, it is important to understand the ozone and population patterns in the region. The peak ozone is found in the eastern basin, in an area with relatively little NO_x, and thus has a high VOC/NO_x ratio. On the other hand, the population is concentrated more in the western basin, in areas with more dense emissions, and in particular NO_x-rich mobile source emissions, and thus having a low VOC/NO_x ratio. Also, the peak ozone is found downwind of the urban area, after the pollutants have had a chance to age, again in contrast to the more densely populated regions that experience fresh emissions. Further, the meteorology (e.g., temperatures and mixing heights) in the two portions of the basin is different. Because of these differences, contrasting the populationweighted ozone impact with the peak ozone impact can help capture the level of difference found from environmental variability. The spatial-exposure metric is expected to give results with characteristics of each of the other metrics.

As shown in Figure B.5, the airshed model-derived spatial and population density weighted results behave similarly to MIRs. The greatest differences are found for formaldehyde and other compounds whose reactivities are highly dependent on photolytic reactions. This may be explained by the use of a reduced photolysis rate in the airshed modeling to account for the observed cloud cover. The box model used clear sky

conditions. The reductions in the reactivities are consistent with the sensitivity to the rate constants for the photolytic reactions (Yang et al, 1995), as addressed in the uncertainty section below. In general, airshed model results for Los Angeles agree well with MIRs, and further show that individual organics have very different ozone impacts. Such a study has not been conducted for other regions.

Russell et al. (1995), Bergin et al. (1995), and Kahn et al. (1998) compared several reactivity metrics for the box and grid models for some two dozen plus compounds including some half dozen aromatics. In general, aromatics turn out to be significantly less reactive or negative, on a relative basis, for some metrics. Since the EPA is moving to an 8 hour ozone standard, this should be the primary metric of choice. It appears as if additional work is needed to look at aromatics under several different conditions. Eastern transport conditions should also be examined in a multiday scenario. A number of the aromatics, important for industrial emissions, may be different on a relative basis.

To further compare the trajectory and airshed model results, regression analysis was performed between the box model reactivities and the airshed reactivities. As shown in Table B.4, Carter's MIR scale corresponded well with the population exposure-based reactivities, and the MOIR scale agreed well with the CIT-S90 peak-ozone sensitivity. In these two cases, the slope of the regression line is virtually 1 (showing little bias as reactivities increase), and the correlation is high. The CIT-S90 spatial exposure metric correlates well with both the MIR and MOIR scales, but shows some bias in the comparison with the MOIR scale, indicating that the spatial exposure metric finds the less reactive compounds to be relatively more reactive than does the MOIR scale.

As seen from Figure B5, there are significant similarities between the CIT-S90 metrics as well, though some differences are evident. Differences were quantified by calculating the normalized bias (a value of 1 would indicate a 100% bias) and standard

deviation between the scales (Table B.5). These differences between potential metrics for reactivity quantification within a modeling study also introduce variability.

A similar issue in regards to the role that environmental variability plays in reactivity quantification is how various meteorological characteristics can affect reactivities. Russell et al. (1995) studied the variability in reactivities as found using the results of the box model of Carter under differing conditions, a similar box model (Yang et al, 1995), and a three-dimensional model (Bergin et al, 1995). First, using just the results of the box model calculations of Carter (1994), they quantified the inter-city variability in the absolute species reactivities along the 39 trajectories, and the inter-city variability in the relative reactivities of the individual VOCs along those same trajectories. Normalized MIRs were calculated by dividing each species city-specific MIR by the geometric mean reactivity of all the species reactivities for that city, and multiplying by the geometric mean reactivity of the 39-city average MIRs. This alleviates the problem that VOCs are generally less reactive, in an absolute sense, in one city versus another. A sample of their results is given below in Table B.6. As seen, the variability in the relative reactivity is significantly reduced between the different trajectories when the relative reactivities are used. Use of relative reactivity generally reduced variability by almost a factor of two, from about 20% to 12%.

More recently, Kahn et al. (1998a,b), Qi et al. (1998) and Yang et al. (1988) also studied spatial variability in VOC reactivity. Kahn et al., (1998a) approached this by applying a three dimensional model to different domains (Los Angeles, Mexico City and Switzerland) that experience very different levels of ozone precursors. Los Angeles has relatively high levels of NO_x in most of the domain, and moderate levels of VOC. Switzerland has lower NO_x and VOC levels. Mexico City has high NO_x levels, and very high VOC levels. While the Los Angeles and Switzerland reactivity results were similar, the Mexico City reactivities varied, suggesting that having a large amount of VOC has a greater impact on compound reactivity than does the level of NO_x. This was further

indicated in the Yang et al., (1998a) study, discussed above, which found that the sensitivity of the relative reactivities to the uncertainties in the VOC emission level was greater than to those in the NO_x level. Yang et al. (1998), also plotted the spatial variation in the VOC reactivities in the Los Angeles basin. Not surprisingly, the relative reactivities do vary (Figure B6). Formaldehyde has its greatest relative reactivity in the source regions since it reacts quickly and is a strong radical source, further increasing VOC oxidation in a NO_x -rich environment. The slower reacting compounds (e.g., pentane) have a proportionally higher relative reactivity downwind. VOCs that can become significant NO_x sinks (e.g., toluene) have the greatest variation in reactivity, going from being positive in the source region to negative far downwind. This spatial variability suggests that it is important to define the endpoint of interest: e.g., peak ozone, ozone exposure, and to calculate the corresponding relative reactivity.

Kahn et al. (1999b) applied the CIT model using the 3-D Decoupled Direct Method (DDM3D) to the U.S.-Mexico border region. This study looked at both the use of direct sensitivity analysis for reactivity assessment, as well as spatial variation in relative reactivity. The use of DDM3D produced similar results to the brute force approach with less computational noise and effort.

In the study by Yang et al., (1998), Monte Carlo analysis was applied with the CIT/DDM3D model, to quantify how influential rate constants, VOC and NO_x emissions and meteorology (i.e., mixing height) impacted the relative reactivity of 11 VOCs. Figure B6 also shows the spatial variability in the coefficient of variation of the HCHO relative reactivity. The uncertainty is relatively uniform at about 35% over the middle of the domain. In addition, multiple linear regression was used to find how individual species' reactivities depended upon model parameters (e.g., rate constants) and inputs (emissions of VOC and NO_x, and mixing heights). For example, the relative reactivities for the ozone exposure to HCHO and pentane were found to be:

$$RR_{HCHO} = 3.0 - 1.5F_{NO_2+h\nu} + 1.4F_{VOC_e} + 2.1F_{HCHO+h\nu} - 0.43F_{PAN-decomp} - 1.1F_{O_3+h\nu\rightarrow O^1D} + 0.9F_{NO_2+HO}$$

$$RR_{pentane} = 0.4 - 0.09F_{O_3+h\nu\rightarrow O^1D} - 0.02F_{VOC_e} - 0.003F_{AFG2+h\nu} - 0.046F_{NO_2+HO} + 0.11F_{AAR2+HO} - 0.058F_{OSD+H_2O} \quad \text{(B3)}$$

The independent variables, the F's, represent the ratio of the variable of interest to the default value, the VOC_e subscript represents the amount that the total VOC emissions were changed, and the other subscripts (e.g., HCHO+hv) represent the corresponding reaction rates. Only the six most important parameters are given. The correlation coefficients in both cases are about 0.80. Both regression and uncertainty analyses suggest that the most influential variables were the formaldehyde photolysis rate, ozone photolysis to O^1D, the NO_2-HO reaction and the VOC emission rate. On the other hand, the mixing height and NO_x emission rate had relatively less impact. It should be noted that these results may be specific to the domain modeled, and should not be generalized to being true for other areas. In fact, it might be suspected that the sensitivity to the VOC emissions rate may be particular to area like Los Angeles, and that would not be the case for a location like Mexico City (high VOC area) or much of the less-urbanized United States (low NO_x), or areas with a larger influence of ozone precursors being transported into the region. This is an obvious area for further exploration.

CHEMICAL MECHANISM UNCERTAINTY

As discussed in the Atmospheric Chemistry section, the chemical mechanisms used in the models to calculate the reactivities of the VOCs have significant uncertainties, which causes a corresponding uncertainty in results of reactivity assessments

Measurement errors in laboratory kinetic and product studies contribute to a minimum level of uncertainty in the mechanisms of even the best studied VOCs, and the reactions of many of the organic compounds emitted into urban atmospheres have never been studied in controlled experiments. Their representation in chemical mechanisms is based on analogy to compounds of similar structure, creating added uncertainty, which is difficult to quantify. At issue is the extent to which the uncertainties in the chemistry impact the calculation of the reactivities for organic compounds.

One way to assess the effects of chemical mechanism uncertainty is to compare reactivity predictions using different mechanisms which represent the same state of the art but which incorporate differing assumptions concerning unknown areas of the chemistry and differing condensation approaches. As discussed above, the SAPRC-90 mechanism was used for calculation of the MIR, MOIR and other reactivity scales because of the number of VOCs it can explicitly represent. The RADM-II mechanism employs assumptions similar to SAPRC-90 concerning uncertain portions of the aromatics and other mechanisms, and would be expected to give similar reactivities for the species that the condensed mechanisms are designed to represent. However, this may not be the case for the Carbon Bond IV (CB4) mechanism, which employs differing assumptions concerning some of the uncertainties in the aromatics mechanisms, and uses different methods for treating alkane and alkene reactions (Gery et al., 1988). Table B.7 shows a comparison of MIR and MOIR (relative to the total base case emissions) calculated with the SAPRC-90 and with a recent version of the CB4 (with minor updates concerning peroxy radical reactions that do not significantly affect ozone predictions (Yarwood, 1994; Carter, 1994b). Other than the mechanism, the scenarios and the calculation methodology are the same (Carter, 1994b). Note that the only compounds shown are those that are either represented explicitly in CB4 or are represented by model species developed based on mechanisms of very similar compounds, so the differences reflect primarily differences in representation of the actual reactions, rather than

condensation effects. Note also that the SAPRC-90 and the CB4 mechanisms were developed around the same time, so they are both based on approximately the same data base of kinetic, mechanistic, and environmental chamber results.

The most conspicuous difference on Table B.7 is for toluene, for which the developers of the CB4 added a speculative reaction so model simulations could accurately predict the relatively low maximum ozone yields in some toluene-NO_x outdoor chamber experiments (Gery et al., 1988). This reaction is not included in the SAPRC-90 mechanism, nor is it in the CB4 mechanism for xylenes. This causes somewhat lower MIR reactivities for toluene and causes toluene to be negatively reactive at the lower NO_x levels where maximum ozone formation occurs. (The SAPRC-90 mechanism also predicts that toluene becomes negatively reactive at low NO_x levels, but the NO_x levels must be much lower than is the case with CB4.) In the case of xylenes, where the CB4 lacks this speculative reaction, the MIR and MOIR relative reactivities agree quite well. The somewhat higher CB4 formaldehyde reactivity is believed to be caused primarily by a greater sensitivity of the CB4 mechanism to radical input processes, rather than by differences in the formaldehyde mechanism itself.

Another way to assess the effects of mechanism uncertainty is to examine changes in calculated reactivities that result when mechanisms are updated. Since SAPRC-90 was developed there has been new kinetic and mechanistic data concerning a number of relevant reactions, and environmental chamber studies of a number of compounds. The effects of two rounds of updates to the SAPRC mechanism on MIR's for selected compounds are shown on Table B.8. The SAPRC-97 mechanism is an updated version of SAPRC-90 which incorporates significant updates in PAN kinetics, major modifications to alkene and aromatic reactions and mechanisms for other individual VOCs resulting from new mechanistic and environmental chamber data (Carter et al, 1997). The SAPRC-98 represents a complete update to the rate constants of the inorganic and common product reactions, somewhat more detailed representation of reactive organic products,

revised estimation methods for OH + alkanes and oxygenates, and re-evaluations against the chamber data (see Carter, 1998 and the Atmospheric Chemistry section.)

Table B.8 shows that updates to the base mechanism can cause a relative MIR change on the order of ~15% even for explicitly represented compounds whose mechanisms were not changed. In the case of going from SAPRC-90 to SAPRC-97, the changes for some of the aromatic isomers is due to new environmental chamber data, and the changes for acetylene and methyl isobutyrate are due to changes in the estimated, unverified mechanisms. (Differences between SAPRC-90 and SAPRC-97 are discussed further below.) In the case of going from SAPRC-97 to SAPRC-98, the relatively large increases in MIR for the higher alkanes, 2-(2- ethoxyethoxy), ethanol and other compounds is due largely to the use of a more reactive model species to represent more reactive non-aldehyde oxygenated products, the changes for acetylene and methyl isobutyrate are due to mechanism revisions resulting from new chamber data, and in the case of the higher ketones the change is due to representing these compounds explicitly rather than by MEK. It can be seen that changes of up to a factor of 3 have occurred for compounds with unverified mechanisms.

More systematic studies of the effects of mechanism uncertainties have been carried out using airshed and box models to explore to what degree uncertainties in chemical rate parameters affect the calculated compound reactivities (Yang et al., 1995; 1996a,b; Bergin et al., 1996; 1997; Wang and Milford, 1998). Figure B7 compares results from box model uncertainty analysis studies conducted by Yang et al. (1996b) using the SAPRC-90 chemical mechanism and by Wang and Milford (1998) using the SAPRC-97 mechanism. Both studies used Monte Carlo analysis with Latin Hypercube Sampling to calculate the uncertainties in MIRs and MOIRs. Computational requirements were reduced by using a single set of trajectory conditions designed by Carter (1994a) to give incremental reactivities close to the average from the 39 trajectories used in developing his scales. Uncertainty estimates for parameters in the SAPRC-90 mechanism were

compiled by Stockwell et al. (1994), largely from concurrent reviews of kinetic data (DeMore et al., 1990; Atkinson et al., 1989). For the SAPRC-97 mechanism, the uncertainty estimates were updated using more recent reviews (DeMore et al., 1994; 1997). In addition, Wang and Milford (1998) rectified a shortcoming of the earlier study by developing original estimates of uncertainties in aromatics oxidation parameters. Aromatics oxidation chemistry is highly uncertain, and the parameters used in chemical mechanisms are estimated by fitting ozone production due to aromatics oxidation in environmental chamber experiments. Accordingly, the uncertainty estimates that Yang et al. (1996a) used for these parameters were very large and highly subjective. Wang and Milford (1998) applied stochastic parameter estimation techniques to the aromatics database from the University of California at Riverside environmental chambers, to objectively assess the uncertainty in the aromatics oxidation parameters.

As shown in Figure B7, mean MIR estimates calculated with SAPRC-97 are generally higher than those calculated with SAPRC-90, reflecting revisions to the mechanism. One exception is the MIR for 1,2,4-trimethylbenzene, which has been adjusted downward based on recent chamber experiments. Yang et al.'s (1996) uncertainty estimates for MIRs ranged from about 30% to 50% of the mean MIR values, for most compounds. Uncertainty estimates for most aromatic compounds fell at the upper end of that range. The recent uncertainty estimates for MIRs made by Wang and Milford (1998) are somewhat lower, ranging from 25% to 35% in most cases. Reduced uncertainty estimates for aromatic compound reactivities suggest that the chamber data effectively constrain the uncertainty in these values. Both studies indicate that uncertainties in MOIRs are somewhat higher than those for MIRs. For SAPRC-97, Wang et al. estimate that uncertainties in MOIRs range from about 30% to 50% for most compounds.

As noted by Yang et al. (1995, 1996b) uncertainties in many rate parameters have similar effects on the reactivities of various compounds, so the resulting incremental

reactivities are strongly correlated. For example, an increase in the photolysis rate for NO2 increases the reactivity of most species by about the same proportion. Thus, the relative reactivity of one species compared to another is not affected as much as the absolute incremental reactivities by chemical parameter uncertainties.

Bergin et al. (1997) extended the box-model rate constant uncertainty studies to a threedimensional model uncertainty study. After the most influential rate parameters were identified by Yang et al. through Monte Carlo simulations, described above, those values in the CIT-S90 model were varied by twice the estimated uncertainty, and the compound reactivity simulations were then recalculated. Results of one metric studied (spatial exposure) are shown in Figure B8. This analysis, again, found that relative reactivities have relatively low sensitivities to rate constant uncertainties. The implication of this result is further demonstrated by considering uncertainties in source reactivity quantification and RAFs. Further analysis of uncertainties using a three-dimensional model was conducted by Yang et al., (1998). As shown in Table B.9, the uncertainties in the local relative reactivity were about 30%, accounting for uncertainties in 14 of the most influential rate constants, VOC and NO_x emissions, and mixing height. Table B.9 rank orders the sources of uncertainty. They found that the major source of uncertainty in quantifying most of the VOC reactivities were the NO_2+HO reaction rate and the VOC emissions rate.

REFERENCES

Altshuller, A. P. and Bufalini, J. J. (1971). *Environ. Sci. Technol, 5:* 39.

Andersson-Skold, Y.; Grenfelt, P.; and Pleije, K. (1992). *J. Air Waste Mgmt. Assoc.*, 42:1152–1158.

AQIRP (1993). *Reactivity Estimates for Reformulated Gasolines and Methanol/Gasoline Blends in Prototype Flexible/Variable Fuel Vehicles,* Technical Bulletin No. 7, Auto/Oil Air Quality Improvement Research Program. Available from the Coordinating Research Council, Atlanta, GA.

Atkinson, R. (1987). *Int. J. Chem. Kinet.,* 19:799–828Atkinson, R. (1990). *Atmos. Environ.,* 24A:1–24

Atkinson, R. (1989). *J. Phys. Chem. Ref. Data,* Monograph No 1.Atkinson, R. (1994). *J. Phys. Chem. Ref. Data,* Monograph No. 2.

Bergin, M.S.; Russell, A.G.; and Milford, J.B. (1995). *Environ. Sci. & Tech.,* 29(12):3029–3037.

Bergin, M.S.; Russell, A.G.; and Milford, J.B. (1998). *Environ. Sci. & Tech.,* 32(5):694–703.

Bowman, F.M. and Seinfeld, J.H. (1994a). *J. Geophys. Res.,* 99:5309–5324.

Bowman, F. M. and Seinfeld, J.H. (1994b). *Atmos. Environ.,* 28:3359–3368.

Bowman, F. M. and Seinfeld, J.H. (1995). *Prog. in Energy and Comb. Sci.* 21:87–417.

Bufalini, J. J.; Walter, T.A.; and Bufalini, M.M. (1977). *Environ. Sci. Technol.,* 11:1181–1185.

CARB. (1989). *Definition of a Low-Emission Motor Vehicle in Compliance with the Mandates of Health and Safety Code Section 39037.05 (Assembly Bill 234,*

Leonard, 1987), Report by Mobile Sources Division, California Air Resources Board, El Monte, CA.

CARB. (1990). *Proposed Regulations for Low-Emission Vehicles and Clean Fuels—Staff Report and Technical Support Document*, Sacramento, CA, August 13. See also Appendix VIII of *California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles*, as last amended September 22, 1993. Incorporated by reference in Section 1960.1 (k) of Title 13, California Code of Regulations.

CARB. (1991). *Proposed Reactivity Adjustment Factors for Transitional Low-Emissions Vehicles— Staff Report and Technical Support Document*, Sacramento, CA, September 27. Andersson-Skold, Y.; Grenfelt, P.; and Pleije, K. (1992). *J. Air Waste Mgmt. Assoc.*, 42:1152–1158.

Carter, W.P.L. (1990). *Atmos. Environ.*, 24A:481–518.

Carter, W.P.L. (1991). *Development of Ozone Reactivity Scales for Volatile Organic Compounds*, EPA 600/3-91-050. U.S. Environmental Protection Agency, Research Triangle Park, NC (August).

Carter, W.P.L. (1994a). *J. Air and Waste Mgmt. Assoc.*, 44:881–899.

Carter, W.P.L. (1994b). *Calculation of Reactivity Scales Using an Updated Carbon Bond IV Mechanism*, Report prepared for Systems Applications International under funding from the Auto/Oil Air Quality Improvement Research Program.

Carter, W.P.L. (1995). *Atmos. Environ.*, 29:2513–2517.

Carter, W.P.L. (1998): "Updated Maximum Incremental Reactivity Scale for Regulatory Applications," Preliminary Report to California Air Resources BoardContract No. 95-308. See http://cert.ucr.edu/~carter/r98tab.htm.

Carter, W.P.L.; Atkinson, R.; Winer, A.M.; and Pitts, J.N. Jr. (1982). *Int. J. Chem. Kinet.*, 14:1071.

Carter, W.P.L. and Atkinson, R. (1989). *Environ. Sci. and Technol.*, 23:864.

Carter, W.P.L. and Lurmann, F.W. (1990). *Evaluation of the RADM Gas-Phase Chemical Mechanism,* Final Report, EPA-600/3-90-001.

Carter, W.P.L. and Lurmann, F.W. (1991). *Atmos. Environ.,* 25A:2771–2806.

Carter, W.P.L.; Pierce, J.A.; Malkina, L; Luo, D.; and Long, W.D. (1993). *Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds,* Report to Coordinating Research Council, Project No. ME-9, California Air Resources Board Contract No. A032-0692; South Coast Air Quality Management District Contract No. C91323, United States Environmental Protection Agency Cooperative Agreement No. CR-814396-01-0, University Corporation for Atmospheric Research Contract No. 59166, and Dow Corning Corporation (April 1).

Carter, W.P.L.; Luo, D.; Malkina, I.L.; and Pierce, J.A. (1995a). *Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NOx*. Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323 (March 24).

Carter, W.P.L.; Pierce, J.A.; Luo, D.; and Malkina, I.L. (1995b). *Atmos. Environ.,* 29:2499–2511.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997): "Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment," final report to California Air Resources Board Contract 92-345, Coordinating Research Council Project M-9, and National Renewable Energy Laboratory Contract ZF-2-12252-07. November 26.

Chameides, W.L.; Fehsenfeld, F.; Rodgers, M.O.; Cardelino, C.; Martinez, J.; Parrish, D.;

Chang, T.Y. and Rudy, S.J. (1990). *Atmos. Environ.* 24A(9):2421-2430.

Chang, T.Y.; Rudy, S.J.; Kuntasal, G.; Gorse, R.A., Jr. (1989). Atmos. Environ. 23(8):1629–1644.

Darnall, K.R.; Lloyd, A.C.; Winer, A.M.; Pitts, J.N. Jr. (1976). *Environ. Sci. Technol.,* 10:692.

Derwent, R.G. and A.M. Hov. (1979). *Computer Modeling Studies of Photochemical Air Pollution Formation in North West Europe*, AERE R 9434, Harwell Laboratory, Oxfordshire, England.

Derwent, R.G. and Jenkin, M.E. (1991). *Atmos. Environ.*, 25(A):1661-1673

Dimitriades, B. (1996): "Scientific Basis for the VOC Reactivity Issues Raised by Section 183(e) of the Clean Air Act Amendments of 1990," J. Air Waste Manage. Assoc. 46, 963-970.

Dodge, M.C. (1977) "Combined Use of Modeling Techniques and Smog Chamber Data to Drive Ozone-Precursor Relationships" in Proceedings, International Conference on Photochemical Oxidant and Its Control, Research Triangle Park, North Carolina, EPA- 600/3-80-028a. Carter, W.P.L. (1990). Atmos. Environ., 24A:481–518.

Dodge, M.C. (1984). *Atmos. Environ.*, 18:1657. In B. Dimitriades, ed., *International Conference on Photochemical Oxidant Pollution and Its Control—Proceedings: Volume II, September 1976*. Research Triangle Park, NC.

Gery, M.W. and Crouse, R.R. (1989). *User's Guide for Executing OZIPR* . Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Jeffries, H.E. and Sexton, K.G. (1993). *The Relative Ozone Forming Potential of Methanol Fueled Vehicle Emissions and Gasoline-Fueled Vehicle Emissions in Outdoor Smog Chambers*, Draft Final Report to the Coordinating Research Council, Project No. ME-1 (September).

Jeffries, H.E. and Crouse, R. (1991). *Scientific and Technical Issues Related to the Application of Incremental Reactivity. Part H: Explaining Mechanism Differences*, Report prepared for Western States Petroleum Association, Glendale, CA (October).

Jiang, W.; Singleton, D.L.; Hedley, M.; and McLaren, R. (1996) *Atmos. Environ.* 31(4):627-638.

Joshi, S.B.; Dodge, M.C.; and Bufalini, J.J. (1982). *Atmos. Environ.*, 16:1301–1310.

Kahn, M.; Yang, YJ; and Russell, A.G. (1997). "Reactivities of Organic Solvents: Comparison between Urban and Regional Domains," Paper No. WA-97-!1540. Presented at the A&WMA Annual Meeting, Toronto, Canada. June. Air & Waste Management Association, Pittsburgh, PA.

Kahn, M., Yang, YJ and Russell, A.G.., (1999a) “Photochemical reactivities of common solvents: comparison between urban and regional domains,” Atmos. Env.

Kahn, M.; Qi , L.; Yang, YJ and Russell, A.G.(1999b) “Regional assessment of relative reactivities using a decoupled, direct method for sensitivity analysis” (to be submitted)

Laity, J.L.; Burstain, F.G.; and Appel, B.R. (1973). In R.W. Tess, ed., *Solvents Theory and Practice,* Adv. Chem. Series, 124:95.

Lonneman, W.; Lawson, D.R.; Rasmussen, R.A.; Zimmerman, P.; Greenburg, J.; Middleton, P.; and Wang, T. (1992). *J. Geophys. Res*., 97:6037.

Lurmann, F.W.; Carter, W.P.L.; and Coyner, R.A. (1987). *A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models. Volume I - Adaptation of the Mechanism,* EPA-600/3-87-014a.

McNair, L.; Russell, A.; and Odman, M.T. (1992). *J. Air Waste Mgmt. Assoc.*, 42:174.

Odman et al., 1994 (URM model) [Odman, M.T., Russell, A.G., (1991). “Multiscale modeling of pollutant transport and chemistry”. *Journal of Geophysical Research* **96**, 7363–7370.]

Russell, A.G.; St. Pierre, D.; and Milford, J.B. (1990). Science 247:201–205.

Russell, A.; Milford, J.; Bergin, M.S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W.R.; and Croes, B. (1995). *Science* 269:491–495

Trijonis, J.C. and Arledge, K.W. (1976). Utility of Reactivity Criteria in Organic Emission Control Strategies: Application to the Los Angeles Atmosphere, EPA/600/3-78/019; TRW/Environmental Services: Redondo Beach, CA.

Weir, B.R.; Rosenbaum, A.S.; Gardner, L.A.; Whitten, G.Z.; and Carter, W. (1988). *Architectural Coatings in the South Coast Air Basin: Survey, Reactivity, and Toxicity Evaluation,* Final Report to the South Coast Management District, SYSAPP-88/137, Systems Applications, Inc., San Rafael, CA (December).

Wilson, K.W. and Doyle, G.J. (1970). *Investigation of Photochemical Reactivities of Organic Solvents,* Final Report, SRI Project PSU-8029, Stanford Research Institute, Irvine, CA (September).

Yang, Y.-J.; Das, M.; Milford, J.B.; Bergin, M.S.; Russell, A.G.; and Stockwell, W.R. (1994). Q*uantification of Organic Compound Reactivities and Effects of Uncertainties in Rate Parameters. An Integrated Approach Using Formal Sensitivity and Uncertainty Analysis and Three Dimensional Air Quality Modeling.* Report prepared for the Auto/Oil Air Quality Improvement Research Program (August).

Yang, Y-J.; Stockwell, W.R.; and Milford, J.B. (1995). *Environ. Sci. & Tech.,* 29(5):1336–1345.

Yang, YJ.; Khan, M.; Wilkinson, J.; and Russell, A.G. (1999) “Spatial uncertainty assessment of relative reactivities” (in preparation)

Yarwood, G. (1994): System Applications, Inc., San Rafael, CA, personal communication with W.P.L. Carter.

TABLES

Table B.1. Summary of compound reactivity modeling studies.

Reference	Model Type	Mechanism	Application
Derwent and Jenkin (1991)	trajectory	Harwell	Two-layer multi-day trajectory simulations of reactivity. Referred to as POCP scales.
McNair et al. (1992)	three-dimensional (CIT)	LCC	Calculation of 3 reactivity scales for 11 lumped compounds. Simulations were performed for a three-day period in the Los Angeles area (the SCAQS episode).
Carter (1994a)	trajectory	SAPRC-90	Development of 18 reactivity scales (including the MIR and MOIR) for 117 compounds. Results are the average of 39 trajectory simulations for 10-hour periods.
Yang et al. (1994)	trajectory and three-D (CIT)	SAPRC-90	Review of rate constant uncertainties and also portions of (Yang et al, 1995; Bergin et al, 1995, 1998). Report.
Yang et al. (1995)	trajectory	SAPRC-90	Rate constant uncertainty calculations for the reactivities of 26 compounds under MIR- and MOIR-type conditions. One averaged trajectory was used rather than the 39 used in the Carter MIR and MOIR calculations.
Bergin et al. (1995)	three-dimensional (CIT)	SAPRC-90	Calculation of 3 reactivity scales for 27 compounds. Simulations were performed for the SCAQS episode.
Jiang et al. (1996)	trajectory	SAPRC-90	Calculation of the contributions of eighteen compounds to ozone concentrations in the Lower Fraser Valley.
Bergin et al. (1997)	three-dimensional (CIT)	SAPRC-90	Rate constant uncertainty calculations for the scales and compounds in the Bergin et al. (1995) study above.
Kahn et al. (1999a)	trajectory and three-dimensional	SAPRC-90	Calculation of solvent reactivities using box and airshed modeling in multiple domains.
Carter (1998)	trajectory	SAPRC-98	Update of Carter (1994)
Kahn et al., (1999b)	three-dimensional	SAPRC-90 (with updates)	Regional uncertainty analysis and use of direct sensitivity method
Yang et al. (1999)	three-dimensional	SAPRC-90 (with updates to 97)	Spatial uncertainty analysis of reactivities

Table B.2. Summary of major characteristics of Carter (1994) reactivity scales.

Scale	Type of Scenarios used	Derivation of scale from individual scenario reactivities	Ozone quantification	Reflects effect of VOC on:
Maximum Incremental Reactivity (MIR)	Low ROG/NO_x conditions where O_3 is most sensitive to VOC changes	Averages of incremental reactivities in the MIR scenarios	Maximum ozone	Ozone formation rates
Maximum Ozone Incremental Reactivity (MOIR)	Moderate ROG/NO_x conditions where highest O_3 yields are formed	Averages of incremental reactivities in the MOIR scenarios	Maximum ozone	Ultimate ozone yield
Equal Benefit Incremental Reactivity (EBIR)	Higher ROG/NO_x conditions where VOC and NO_x control are equally effective in reducing O_3	Averages of incremental reactivities in the EBIR scenarios	Maximum ozone	Ultimate ozone yield
Base-Case Average Ratio: O_3 Yield	Base case conditions (ROG/NO_x conditions are as observed for the individual scenarios)	Averages of incremental reactivities in the base case scenarios	Maximum ozone	Ultimate ozone yield
Base-Case Least Squares Error: O_3 yield.	Base-Case	Minimizes change in ozone if a "null test" substitution were made using the scale[a]	Maximum ozone	Depends on the variability of scenario conditions[b]
Base-Case Average Ratio: Integrated O_3	Base-Case	Averages of incremental reactivities in the base case scenarios	Integrated ozone	Ozone formation rate and ultimate yield
Base-Case Least Squares Error—Integrated O_3	Base-Case	Same as base case least squares error — O_3 yield.[b]	Integrated ozone	Ozone formation rate

[a] A "null test" substitution based on a reactivity scale consists of substituting VOC emissions such that the scale predicts there would be no change in ozone.

[b] Depends on effect on O_3 formation rate if scenarios are highly varied in ROG/NO_x conditions .

Table B.3. Summary of source emissions reactivity modeling studies.

Reference	Model Type	Mechanism	Application
Trijonis and Arledge (1976)	calculated (not modeled)	EPA Smog Chamber Data	Estimated major source reactivities for metropolitan Los Angeles.
Chang et al. (1989)	trajectory	LCC	Methanol fuel vehicle impacts with respect to conventionally fueled vehicles.
Russell et al. (1990)	three-dimensional (CIT)	LCC	Potential methanol fuel vehicle impacts for the SCAQS episode (compared to equal mass emissions from conventional vehicles).
McNair et al. (1994) (100)	three-dimensional (CIT)	LCC	Calculations of RAFs for 4 fuels. Simulations were performed for the SCAQS episode.
Yang et al. (1996) (101, 102)	trajectory	SAPRC-90	Rate constant and exhaust composition uncertainty calculations for the RAFs from reformulated gasolines and methanol.
Bergin et al. (1996) (103)	trajectory and three-dimensional (CIT)	SAPRC-90	Report on box model study described above (101, 102) and a 3D study of the effects of rate constant and product yield uncertainties on predicted ozone impacts of 5 alternative fuel RAFs.
Russell et al. (1995) (96)	trajectory and three-dimensional (CIT)	SAPRC-90	Evaluation of combined results of most previous studies (82, 84, 85, 100, 101, 103). An economic analysis was also performed.
Guthrie et al. (1996) (104)	three-dimensional (UAM)	CB4	Modeling of potential impacts of the use of three alternative fuels (CNG, M85, and RFG) in two urban areas. Report.

Table B.4. Regression results for airshed model exposure vs. MIR and airshed peak ozone vs. MOIR measures (Bergin et al., 1996, 1998).

Comparison	R^2	Slope	Intercept
Population Exposure to MIR	0.81	0.88	0.04
Spatial Exposure to MIR	0.97	0.98	0.04
Peak to MOIR	0.80	1.01	0.05
Spatial Exposure to MOIR	0.96	1.09	-0.06

Table B.5. Normalized bias and standard deviation between reactivity metrics calculated using the CIT-S90 airshed model (Bergin et al., 1996, 1998)

Comparison	Bias	Standard
Population to Spatial Exposure	-0.21	0.22
Peak Ozone to Spatial Exposure	0.22	.052
Peak Ozone to Population Exposure	0.39	0.67

Table B.6. Example MIRs and variations between locations (mean and standard deviation) (Russell et al., 1995)

Compound	Mean reactivities across 39 cities (Non-normalized/Normalized)	Standard deviation (Non-normalized/Normalized)
HCHO	7.2/7.1	1.0/0.58
Methanol	0.56/0.55	0.11/0.064
Ethane	0.25/0.24	0.070/0.045
Toluene	2.7/2.7	0.52/0.28
Pentene	6.2/6.1	1.2/0.64

Table B.7. Comparision of relative reactivities calculated using the SAPRC90 and the Carbon Bond 4 mechanisms.

Compound	Reactivity relative to base ROG mixture (mass basis)					
	MIR			MOIR		
	S-90	CB4	Diff	S-90	CB4	Diff
n-Hexane	0.31	0.35	10%	0.53	0.57	7%
Ethene	2.31	2.42	5%	2.61	2.76	6%
Propene	2.98	3.48	14%	3.11	3.66	15%
trans-2-Butene	3.15	3.13	-1%	3.10	3.28	5%
Toluene	0.86	0.57	-52%	0.52	-0.19	378%
m-Xylene	2.58	2.62	1%	2.02	2.04	1%
Formaldehyde	2.26	2.81	19%	1.72	2.21	22%
Acetaldehyde	1.75	1.99	12%	1.79	2.09	14%
Methylethy ketone	0.37	0.28	-35%	0.45	0.46	1%
Methanol	0.18	0.19	5%	0.23	0.23	2%
Ethanol	0.42	0.42	-1%	0.60	0.61	2%

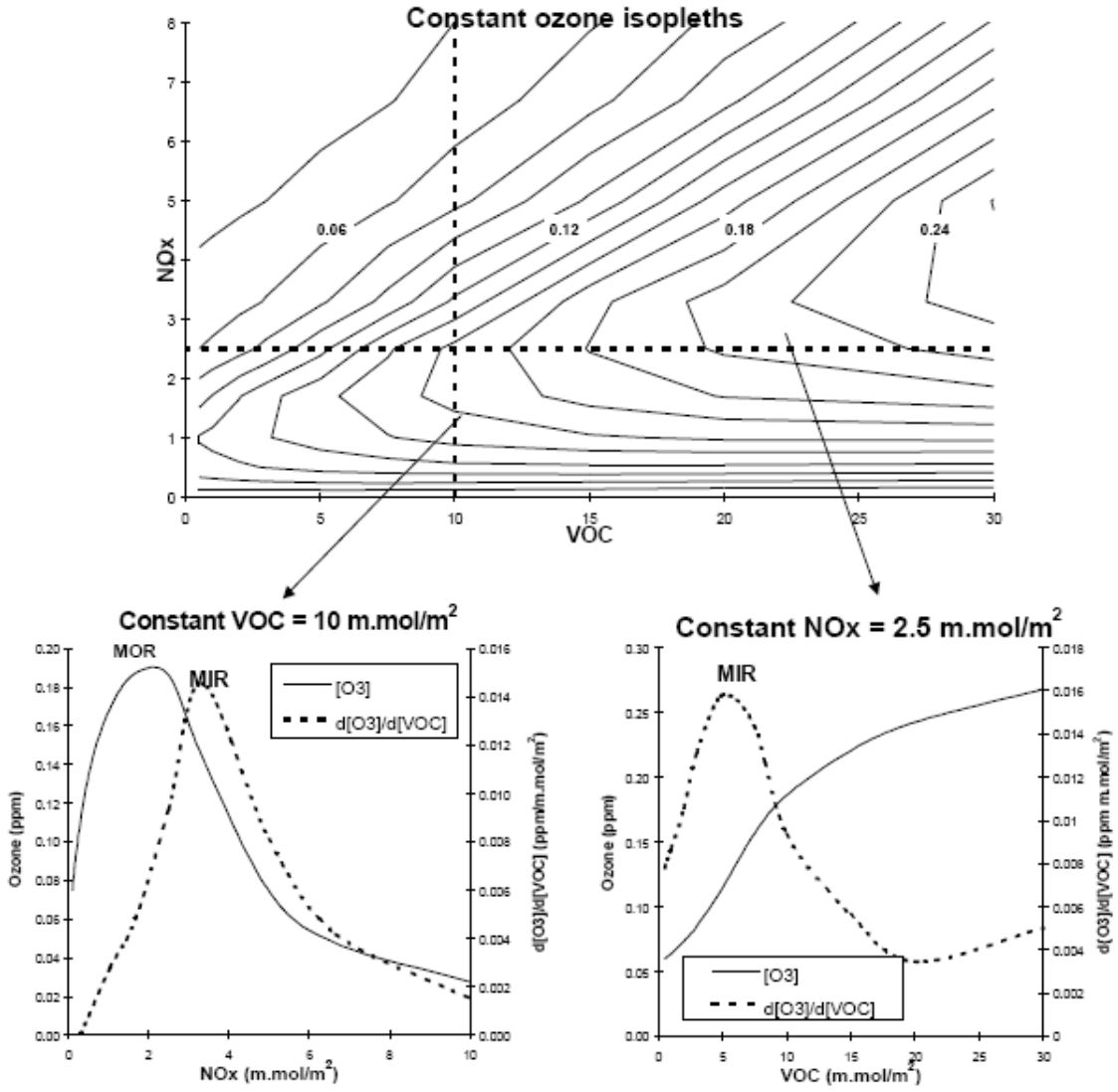
Table B.8. Effect of SAPRC mechanism updates on calculated MIR's.

Compound	Reactivity relative to base ROG mixture (mass basis)					
	SAPRC Version			Change		
	90	97	98	90->97	90->98	97->98
Ethane	0.08	0.08	0.09	0%	15%	15%
n-Octane	0.19	0.17	0.32	-12%	63%	84%
n-Pentadecane	0.09	0.09	0.15	-8%	58%	71%
2,4-Dimethyl Heptane	0.42	0.44	0.51	5%	20%	15%
Ethene	2.31	2.05	2.53	-11%	9%	23%
Propene	2.98	2.72	3.18	-9%	7%	17%
1-Hexene	1.40	1.40	1.61	0%	15%	15%
trans-2-Butene	3.15	3.24	3.76	3%	19%	16%
Isoprene	2.87	2.30	2.93	-20%	2%	27%
a-Pinene	1.04	0.96	1.29	-8%	24%	35%
Toluene	0.86	1.26	1.06	46%	23%	-16%
p-Xylene	2.09	0.71	1.12	-66%	-46%	58%
m-Xylene	2.58	3.49	2.82	35%	9%	-19%
1,3,5-Trimethyl Benzene	3.20	3.37	2.83	5%	-12%	-16%
1,2,4-Trimethyl Benzene	2.80	1.31	1.90	-53%	-32%	45%
Naphthalene	0.37	0.31	0.78	-17%	109%	150%
Acetylene	0.16	0.09	0.31	-45%	94%	256%
Ethanol	0.42	0.42	0.49	-1%	15%	15%
Propylene Glycol	0.49	0.61	0.67	24%	38%	11%
Methyl t-Butyl Ether	0.20	0.18	0.34	-10%	72%	91%
2-(2-Ethoxyethoxy) EtOH	0.41	0.59	0.99	43%	139%	67%
Methyl Isobutyrate	0.06	0.18	0.11	196%	72%	-42%
Formaldehyde	2.26	1.62	2.33	-28%	3%	44%
C3 Aldehydes	2.07	1.85	2.13	-11%	3%	15%
Acetone	0.18	0.12	0.12	-33%	-31%	2%
C6 Ketones	0.27	0.23	0.94	-13%	251%	304%

TableB9. Rank ordering and source attribution of uncertainty in relative reactivities for airshed modeling of Los Angeles.

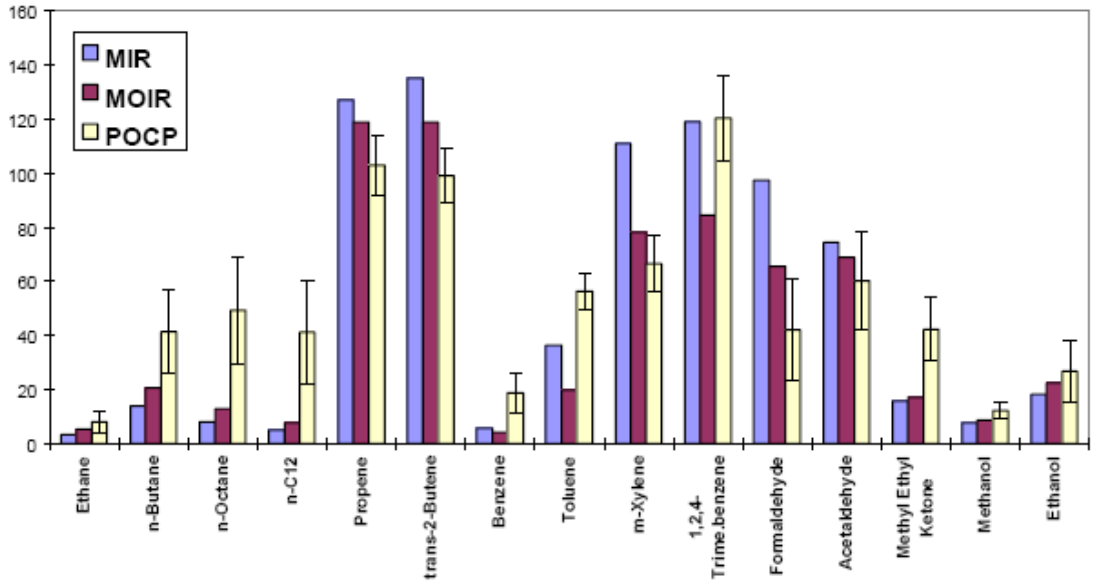
Parameter	**Relative Reactivity, Uncertainty and Contributions to Relative Reactivity Uncertainty**		
	HCHO	Pentane	Average over 11 VOCs
Overall Relative Reactivity/ uncertainty/COV	5.76/1.05/0.26	0.42/0.051/0.12	$COV_{average}$=0.19+/-0.09
Paramter		**Uncertainty Contributions**	
NO2+hv	0.085	0.024	0.03
O3+NO	0.016	0.019	0.01
O3+hv-->O^1D	0.084	0.19	0.05
O^1D+H2O	0.011	0.076	0.03
O^1D+M	0.043	0.043	0.02
HO +NO2	0.079	0.173	0.19
HO2+NO	0.006	0.022	0.01
RO2R+NO	0.005	0.006	0.02
AFG2+hv	0.009	0.057	0.12
CCO+NO	0.039	0.035	0.12
CCO+NO2	0.034	0.038	0.08
PAN decomposition	0.073	0.022	0.08
HCHO+hv	0.276	0.11	0.13
AAR2+HO	0.044	0.035	0.01
NOx Emissions	0.004	0.002	0.006
VOC Emissions	0.182	0.051	0.08
Mixing Height	0.011	0.094	0.04

FIGURES



[1]MOR, moximum ozone reactivity, also referred to as maximum ozone incremental reactivity (MOIR); MIR, maxium incremenmtal reactivity.
One day maximum ozone concentrations calculated in a one-day box model simulation using the "averaged conditions" scenario of Carter (1994) and the SAPRC-93 chemical mechanism.

Figure B1. Dependence of peak ozone and $d[O_3]/d[VOC]$ on VOC and NO_x.



[1] **Incremental reactivities (ozone per gram) are shown relative to ethene = 100. MIR and MOIR reactivities from Carter (23). POCP reactivities are averages for various trajectories calculated by Derwent and Jenkin (81), with the error bars being the standard deviation of the averages.**

Figure B2. Comparison of MIR, MOIR, and POCP relative reactivities.

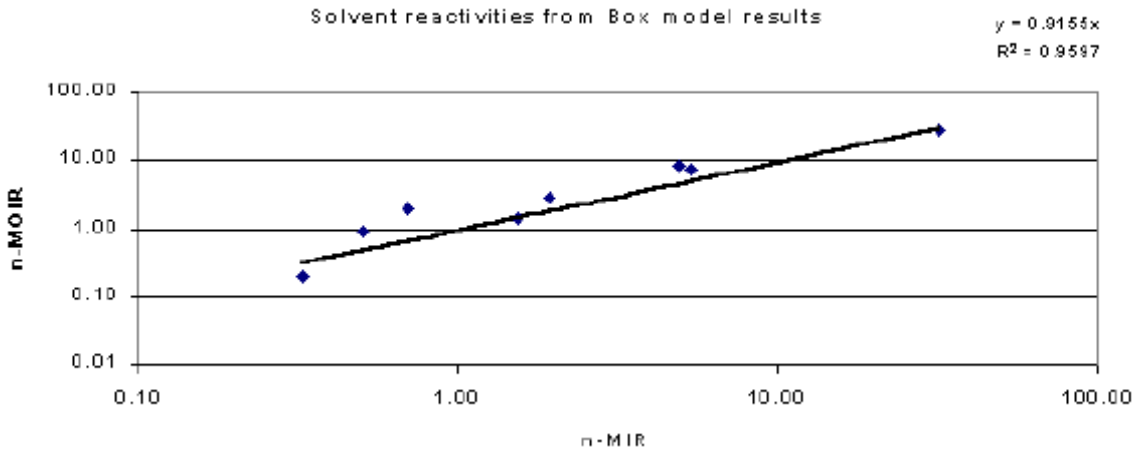


Figure B3. Relative (normalized) N-MIR and N_MOIR reactivities for six solvents (Kahn et al., 1997).

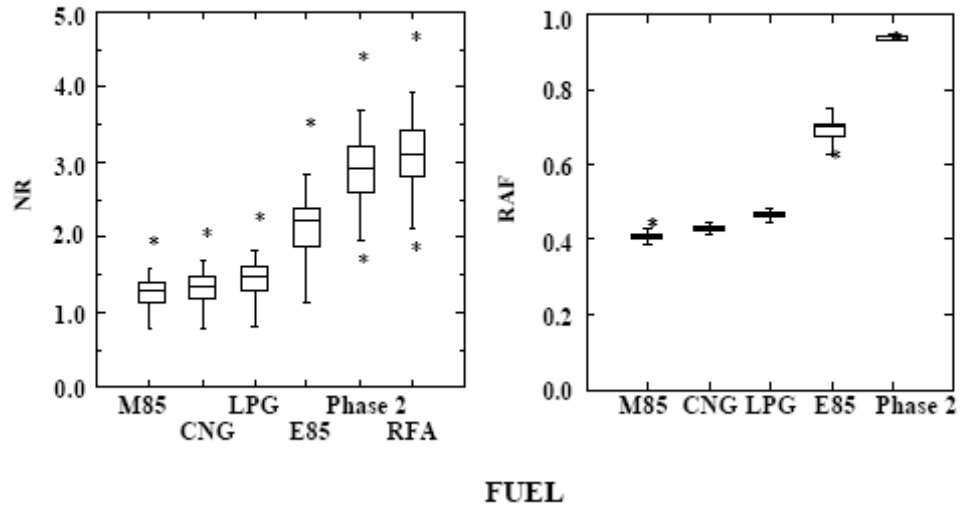


Figure B4. Box plots of the calculated (a) net reactivities (NRs) and (b) normalized reactivities (RAFs) across cities (Russell et al., 1995).

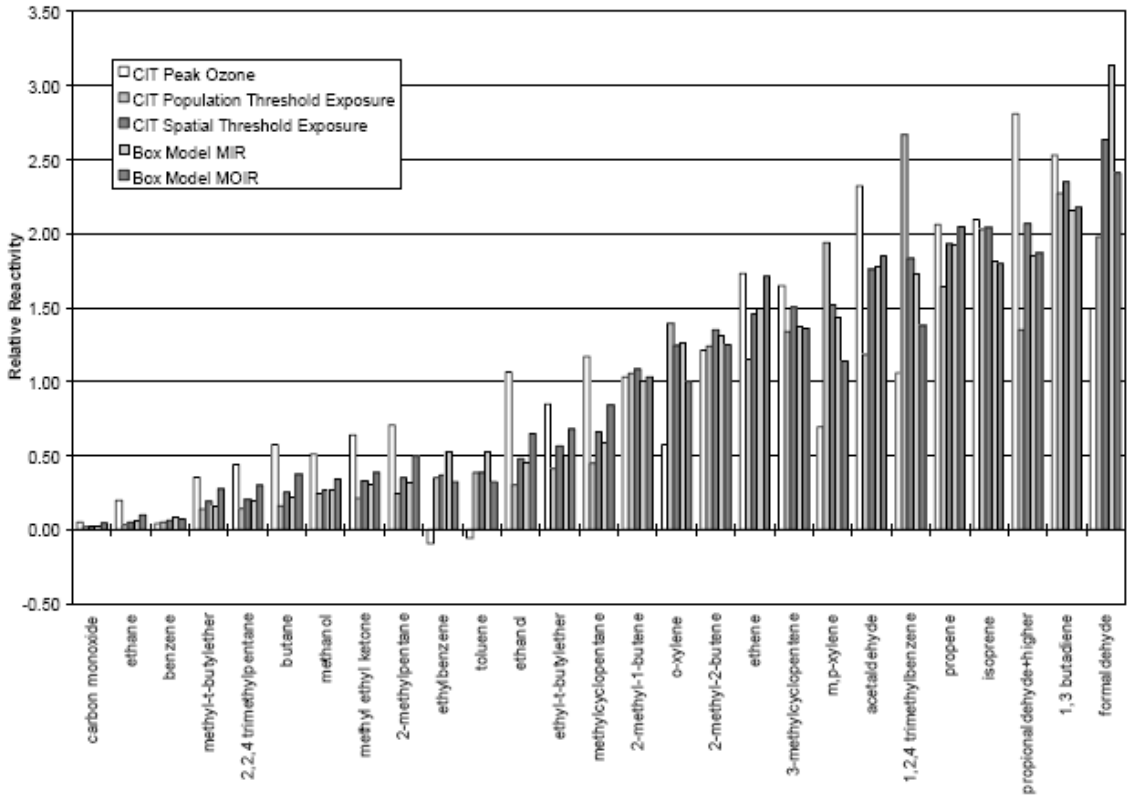
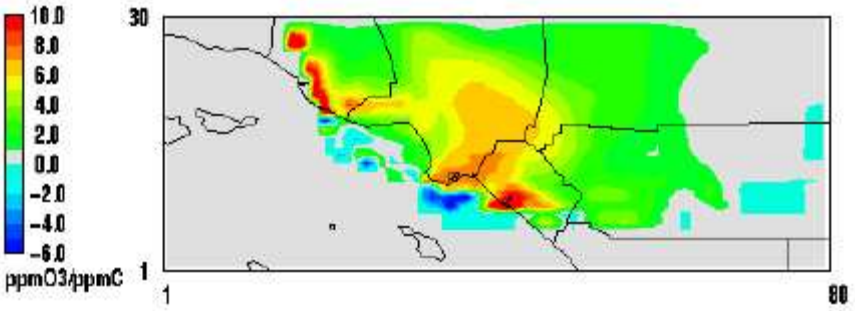
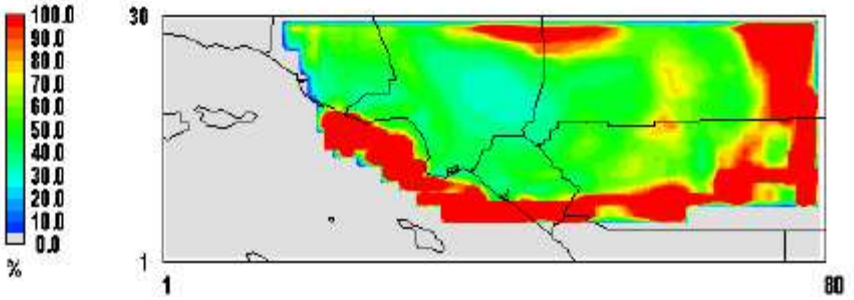


Figure B5. Comparison of three-dimensional and trajectory modeled relative reactivities.



a. Normalized HCHO Relative Reactivity (ppmO3/ppmC) at 1400 hour, August 29, 1987 in the Los Angeles, CA area.



b. Coefficient of variation (relative uncertainty) (%) of the HCHO Relative Reactivity at 1400 hour, August 29, 1987.

Figure B6. Spatial distribution of relative reactivities (Yang et al., 1999).

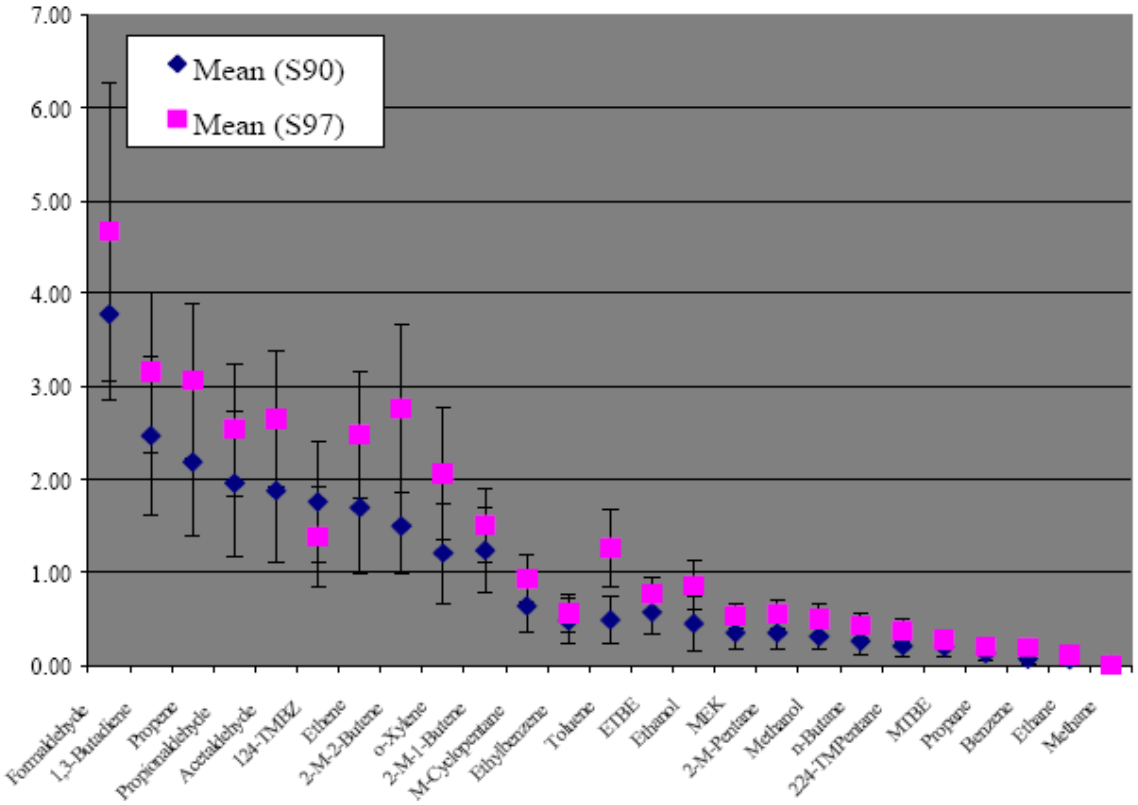


Figure B7. Mean values and 1s uncertainties of MIRs for selected organic compounds, calculated with the SAPRC90 and SAPRC97 mechanisms.

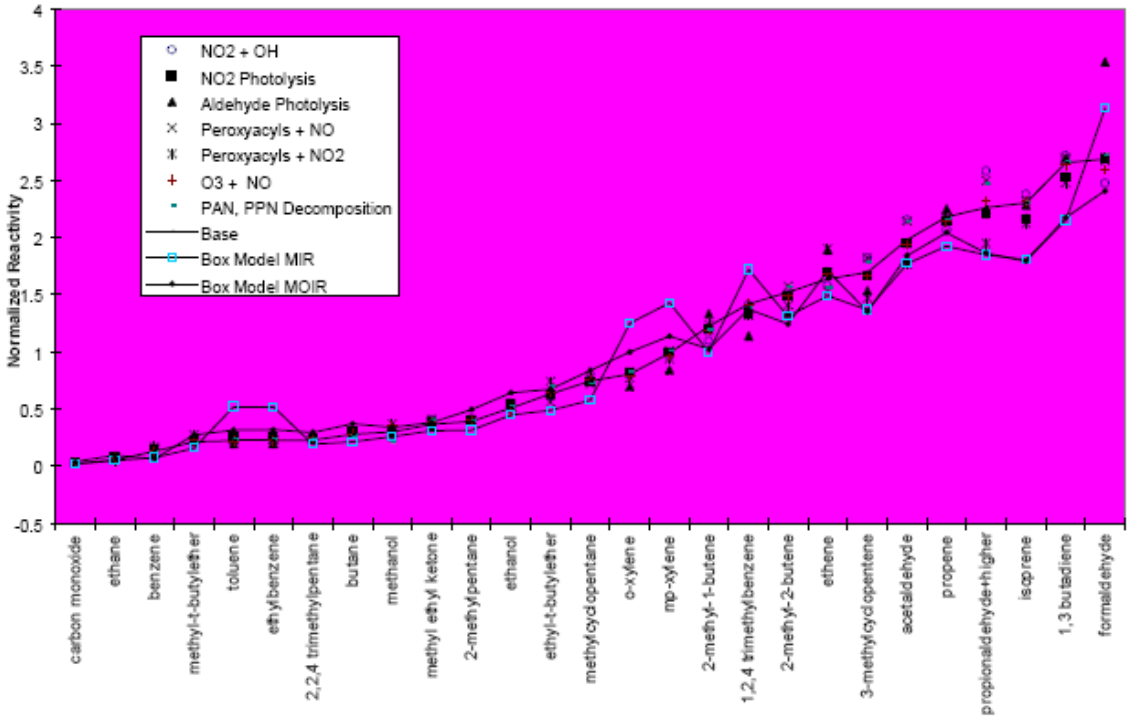


Figure B8. Spatial exposure normalized reactivity predictions from rate constant uncertainty adjustments (Bergin et al., 1998)

Appendix C.

Hakami, A., M.S. Bergin, and A.G. Russell, **2004**. "Ozone formation potential of organic compounds in the eastern United States: A comparison of episodes, inventories, and domains", *Environmental Science & Technology*, **33**(24), 6748-6759.

Environ. Sci. Technol. 2004, 38, 6748−6759

Ozone Formation Potential of Organic Compounds in the Eastern United States: A Comparison of Episodes, Inventories, and Domains

AMIR HAKAMI,† MICHELLE S. BERGIN,‡ AND ARMISTEAD G. RUSSELL*,‡

Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, California 91125, and School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0512

Direct sensitivity analysis is applied for 3-D assessment of ozone reactivity (or ozone formation potential) in the Eastern United States. A detailed chemical mechanism (SAPRC-99) is implemented in a multiscale air quality model to calculate the reactivity of 32 explicit and 9 lumped compounds. Simulations are carried out for two different episodes and two different emission scenarios. While absolute reactivities of VOCs show a great deal of spatial variability, relative reactivities (normalized to the reactivity of a base mixture) produce a significantly more homogeneous field. Three types of domain-wide relative reactivity metrics are formed for 1-h and 8-h averaging intervals. In general, ozone reactivity metrics (with the exception of those based on daily peak ozone) are fairly robust and consistent between different episodes or emission scenarios. The 3-D metrics also show fairly similar rankings for VOC reactivity when compared to the box model scales. However, the 3-D metrics have a noticeably narrower range for species reactivities, as they result in lower reactivity for some of the more reactive, radical-producing VOCs (especially aldehydes). As expected, episodes and emission scenarios with less radical availability have higher absolute reactivities for all species and higher relative reactivities for the more radical-producing species. Finally, comparing the results with those from a different domain (central California) shows that relative reactivity metrics are comparable over these two significantly different domains.

Introduction

Maintaining ozone concentrations at the levels prescribed by health and environmental standards or guidelines has been one of the main challenges facing air quality management agencies throughout the world. In the Unites States, ozone attainment has become even more of a challenge in light of the new and more stringent 8-h standards. As a secondary pollutant, ozone control strategies rely on reducing the emissions of its precursors: oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). VOC-based control strategies have historically treated organic emissions on a mass basis and without distinction among compounds. However, each organic compound leads to ozone production through different paths and by varying rates. Consequently, there have been efforts to rank organic compounds based on their ozone formation potential (usually referred to as reactivity) and to incorporate these rankings into the policy-making process as a means of developing more cost-effective control strategies (*1*, *2*). Recognizing the possible benefits and increased flexibility for industries and regulators, California has adopted reactivity-based regulations for controlling VOC emissions from gasoline vehicles and aerosol coating processes (*3*, *4*).

Carter applied a comprehensive chemical mechanism in a box model to calculate organic reactivities for chemical conditions similar to 39 cities in the United States (*5*). Among the various box model scales developed by Carter, Maximum Incremental Reactivity (MIR) and Maximum Ozone Incremental Reactivity (MOIR) are the most widely used. Incremental Reactivity (IR) of an organic compound is defined as

$$IR_i = \lim_{\Delta VOC_i \to 0} \left(\frac{\Delta O_3}{\Delta VOC_i} \right) \quad (1)$$

where changes in VOC and O_3 are compared to a basecase box model simulation. NO_x availability is the most important factor affecting the incremental reactivity of different VOCs. Therefore, MIR and MOIR scales were calculated for each scenario (city) based on NO_x adjustment methods (*5*, *6*). In the MIR scenario, the NO_x initial concentration in the box model is adjusted such that the ozone concentration at the end of simulation (10 h) is most sensitive to VOC addition. These conditions are typical of NO_x-inhibited urban or industrial plumes, where VOC control is most effective. The MOIR scale is calculated by adjusting NO_x levels to produce the maximum ozone concentration. The MOIR conditions represent lower NO_x levels than MIR and happen when the sensitivity of ozone to NO_x levels is zero.

Box model reactivity scales have inherent limitations, and, therefore, their application as a policy-making tool has been subject to scientific debate. In other words, the robustness of the reactivity scales in various atmospheric conditions is a major question to be addressed before reactivity scales can be widely adopted as a policy-making tool. A number of investigators have applied 3-D air quality models for reactivity assessment (*1*, *2*, *7*−*9*). Most recently, an updated chemical mechanism (SAPRC-99) (*6*) and formal sensitivity analysis have been used for 3-D reactivity assessment in California (*10*−*12*). The prevalent conclusion from previous research has been that 3-D VOC reactivities, when calculated on a relative basis, are comparable to box model scales. These studies, however, have been mostly limited to urban or small regional domains or small and condensed chemical mechanisms. Robustness of reactivity scales can be better tested when a detailed chemical mechanism is applied in large domains, where greater variability in chemical regimes and/or environmental conditions exists.

In this study, an air quality model using the SAPRC-99 chemical mechanism and the 3-D decoupled direct method (DDM-3D) (*13*) for sensitivity analysis is applied to the eastern half of the United States to assess VOC reactivities. SAPRC is the recommended chemical mechanism for reactivity assessment (*14*), and DDM is most suitable for calculation of incremental reactivities (i.e., partial derivatives as opposed to finite difference approximations). To examine the effect of different meteorological or environmental factors on 3-D reactivities, two multiday episodes, each with two different

* Corresponding author phone: (404)894-3079; fax: (404)894-8266; e-mail: trussell@ce.gatech.edu.
† California Institute of Technology.
‡ Georgia Institute of Technology.

10.1021/es035471a CCC: $27.50
Published on Web 11/16/2004

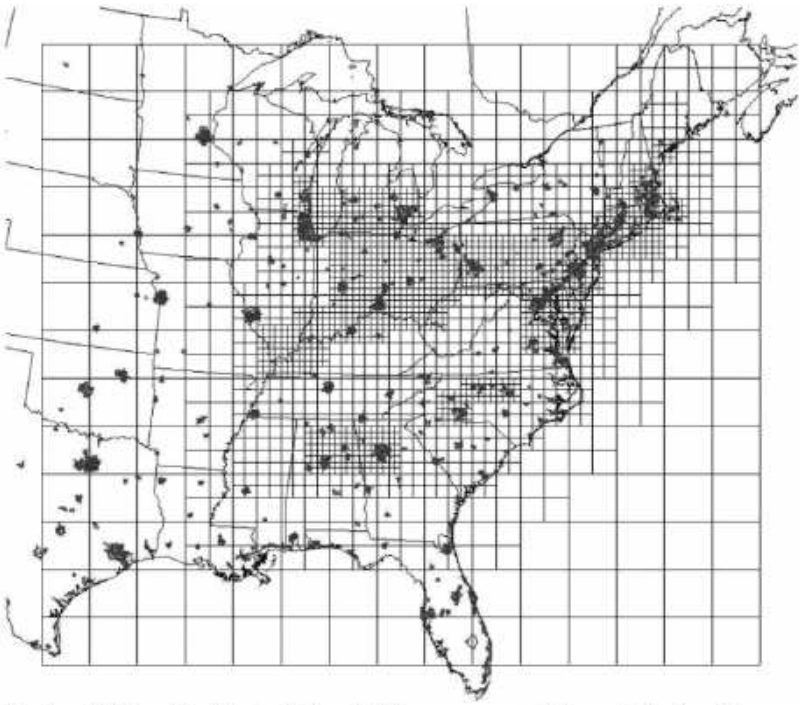


FIGURE 1. The multiscale grid designed for this study. The shaded areas represent high population densities.

TABLE 1: URM-1ATM Specifications

chemistry	SAPRC-99
number of species	102
steady-state species	7
explicit VOCs	42
number of reactions	252
number of photolytic reactions	31
chemical solver	hybrid (*18*)
horizontal transport	finite element scheme
advection scheme	PPM (*19*)
emissions	modeled using EMS-95
number of emitted species	39

emission scenarios (basecase and future), are simulated. The results are also compared to those from a previous California study (*12*).

Method

Model and Inputs. An updated version of the Urban-to-Regional Multiscale (URM) (*15*), with DDM-3D and SAPRC-99 is used for 3-D reactivity assessment over the eastern United States. URM is an Eulerian 3-D photochemical air quality model that accounts for gas-phase chemistry, aerosol dynamics, clouds, and precipitation processes (*16*). It applies multiscale gridding, which differs from nested gridding in that all grids are integrated as one continuous domain. The multiscale grid used for this study is shown in Figure 1 (*17*). The domain consists of 24, 48, 96, and 192 kilometer grids and with 7 vertical nonuniform layers. The finest grids are extended over the major urban or industrial emission sources. Table 1 gives an overview of URM-1ATM model. Other details of the modeling are available elsewhere (*20*).

Reactivity simulations were carried out for two distinct meteorological episodes, May 22−27, and July 10−18, 1995, using day-specific emissions inventories corresponding to both the base year (1995) and a future year, 2010. Meteorologically, the May episode is less conducive to ozone formation and leads to moderate ozone levels, while the July episode was very favorable to ozone formation in much of the eastern United States (*17, 20*). These two episodes are chosen to examine the impact of meteorology on reactivities. Similarly, the future inventories are used to evaluate the effect that emission controls have on organic reactivities. Future inventories used in this study do not account for changes in biogenic emissions as a result of modified land use. Table 2 shows the average daily emissions in the four episodes. Excluding the "ramp-up" days (used to remove the effect of initial conditions), 5 and 8 days of simulations results are available for the May and July episodes, respectively.

DDM Sensitivity Analysis. 3-D air quality models numerically solve the Atmospheric Diffusion Equation (ADE)

$$\frac{\partial C_i}{\partial t} = -\nabla\cdot(\mathbf{u}C_i) + \nabla\cdot(\mathbf{K}\nabla C_i) + R_i + E_i \qquad (2)$$

where **u** is the three-dimensional wind field, and **K** is the turbulent diffusivity tensor. C, E, and R are the grid cell average concentration, emission rate, and chemical reaction rate of species i, respectively. These equations are solved using the method of operator splitting and are subject to specific initial and boundary conditions (*21*).

DDM sensitivity technique (*22, 23, 13*) solves the sensitivity equations that correspond to the ADE, using the same structure and numerical routines. Sensitivity equations are derived by differentiating the ADE with respect to the sensitivity parameter. For reactivity assessment, the sensitivity parameter of concern is the emission rate of each individual organic compound, E_j. Differentiation of eq 2 results in

$$\frac{\partial S_{ij}}{\partial t} = -\nabla\cdot(\mathbf{u}S_{ij}) + \nabla\cdot(\mathbf{K}\nabla S_{ij}) + \mathbf{J}\mathbf{S}_j + E_j\delta_{ij} \qquad (3)$$

where S_{ij} is the seminormalized sensitivity of species i to the emission of species j (in this case a VOC). $\mathbf{S}_j$ is the row vector of sensitivity coefficients, **J** is the Jacobian matrix of the

TABLE 2: Average Daily Domain-Wide Emissions for Different Episodes (Tons per Day)

	NO_x sources				VOC sources			
	biogenics	mobile	point	area	biogenics	mobile	point	area
July 1995	5100	21300	30200	3000	176200	20600	8800	18300
July 2010	5100	14700	15300	3300	176200	13500	6600	16000
May 1995	3000	19900	24600	5700	78400	17000	7900	19100
May 2010	3000	13200	14300	6000	78400	10700	6200	17300

reaction rates ($J_{ik} = \partial R_i/\partial C_k$), and δ_{ij} is the Kronecker delta function. The form of eq 3 is similar to the ADE, and the linear processes (transport, deposition, and emissions) can be integrated by the same numerical routines. The nonlinear chemistry becomes a linear system of sensitivity coefficients (when decoupled from concentrations) and is solved accordingly. In comparison to the traditional brute-force method (one-at-a-time perturbation of sensitivity parameter), direct sensitivity techniques are computationally more efficient and less prone to numerical inaccuracies.

Reactivity Assessment and Metrics. Absolute incremental reactivities are calculated by including emissions of each target VOC in eq 3, leading to an additional set of sensitivity equations being integrated using DDM-3D. This uses the nature of DDM being decoupled such that the concentration field remains unaffected. To readily compare the reactivity of different compounds, VOC emissions for each target VOC in eq 3 are perturbed equally on a mass basis and are specified as a fraction of the total anthropogenic VOC emissions:

$$E_j = \alpha \sum_k E_k \tag{4}$$

The resulting sensitivity coefficient ($\partial C_{O_3}/\partial E_{VOC_j}$) from eq 3 is the absolute incremental reactivity of organic compound j. However, it is usually the relative importance (or ranking) of each VOC in comparison with the others that is of more practical significance. Knowing the relative importance (or ranking) of different VOCs allows for targeting the more reactive compounds, hence more efficient and flexible control strategies. It is also shown that relative reactivities exhibit lower temporal and spatial variability than the absolute values (*1, 12*). Three-dimensional Relative Incremental Reactivities are defined as

$$\mathrm{RIR}_i = \frac{\mathrm{IR}_i}{\overline{\mathrm{IR}}_{\mathrm{Base}}} \tag{5}$$

where IR_i is the 3-D absolute reactivity of species i (in units of ppm O_3/g VOC) calculated from three-dimensional modeling (S_{ij} in eq 3), and $\overline{\mathrm{IR}}_{\mathrm{Base}}$ is the absolute reactivity of a base VOC mixture

$$\overline{\mathrm{IR}}_{\mathrm{Base}} = \sum_{j=1}^{N} y_j IR_j \tag{6}$$

where N is the total number of VOCs in the mixture and y_i is the mole fraction (per mole of carbon of the base mixture) for each organic compound in the base mixture. The mixture composition is usually chosen to represent an average mixture of organic compounds based on a source or receptor profile. For this study the mixture is based on an emission profile calculated from the total U.S. emissions, and its composition is shown in Table 3.

Unlike typical box model scales, 3-D reactivities are based on spatially and temporally varying perturbations in emissions. Therefore, translating the 3-D reactivity values into a single measure of ozone formation potential is more complicated than for the box model. The problem is further compounded by the fact that in a large domain, each air mass can be subject to different environmental conditions and may exhibit significantly different behavior. For policy-making applications, however, it is desirable to find an ensemble measure to compare different VOCs in terms of their ozone formation potential.

TABLE 3: Composition of the Base Reactivity Mixture (*24*)

species or group	moles/mole-C
ethane	8.68e-3
ALK2[a]	7.16e-3
n-butane	1.50e-2
ALK4[b]	3.51e-2
ethene	2.23e-2
lumped olefins	1.16e-2
2-methyl 2-butene	4.56e-3
butadiene	1.36e-3
isoprene	3.77e-4
α-pinene	7.23e-4
benzene	7.25e-3
toluene	1.29e-2
m-xylene	7.04e-3
CRES[c]	8.92e-4
formaldehyde	9.86e-3
acetaldehyde	2.16e-3
propionaldehyde	1.68e-3
benzaldehyde	1.05e-3
acetone	4.66e-3
methyl ethyl ketone	4.56e-3
inert	7.77e-3
acetylene	5.30e-3
methanol	9.09e-3
methyl *tert*-butyl ether	5.07e-3
n-butyl acetate	3.71e-2
ethanol	2.12e-2
acrolein	1.21e-3

[a] ALK2 is 0.5 (ethane + *n*-butane). [b] ALK4 is 0.25 (methylcyclopentane + isopentane + *n*-pentane + 2,2,4-trimethylpentane). [c] CRES is 0.5 (toluene + benzaldehyde).

In this study three different types of 3-D relative reactivity metrics are defined and used. 3-D maximum incremental reactivity (MIR-3D) metric is defined as the 1-h RIR of each species, at the time and location where the base mixture has its daily maximum reactivity. Peak ozone incremental reactivity (POIR-3D) is defined as the 1-h RIR of each species at the time and location of the daily peak ozone concentration. MIR-$3D_{8h}$ and POIR-$3D_{8h}$ metrics are calculated in the same manner but for 8-h averaging periods. The nomenclature for POIR metrics is used to distinguish it from the box model MOIR scales. MIR-3D is expected to represent a similar chemical regime to the box model MIR. However, POIR will not necessarily happen at the time and location where ozone sensitivity to NO_x emissions is zero, which is the required condition for the box model MOIR. A Least-Square Relative Reactivity (LS-RR) metric (*9*) is calculated as the slope of the line that represents the absolute reactivity of each species versus the reactivity of the base mixture. This metric is calculated for grid cells and times with ozone concentrations and base mixture reactivities above a set threshold value

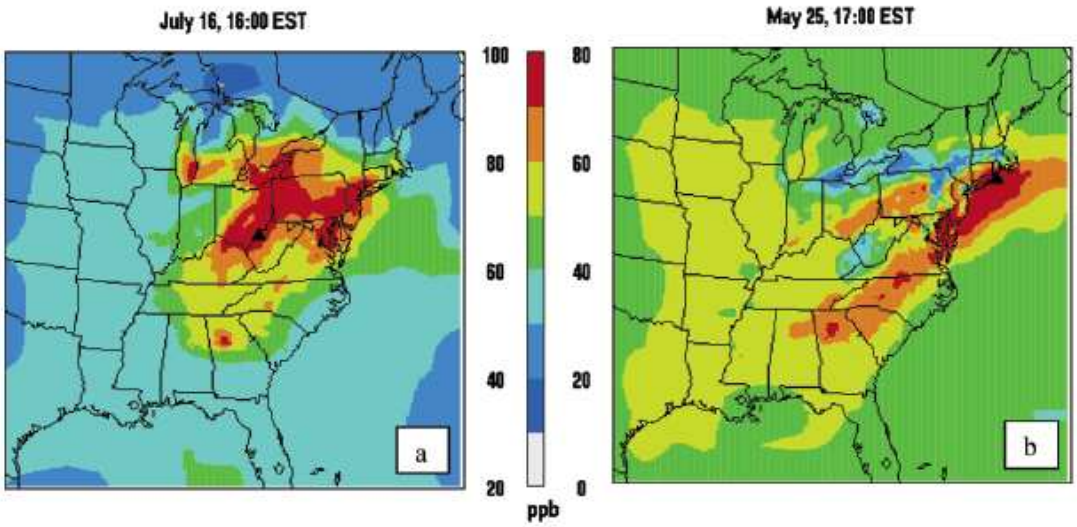


FIGURE 2. Ozone concentrations at the time of peak for (a) July 1995 and (b) May 1995. Peak locations are marked. Note different scales for parts (a) and (b).

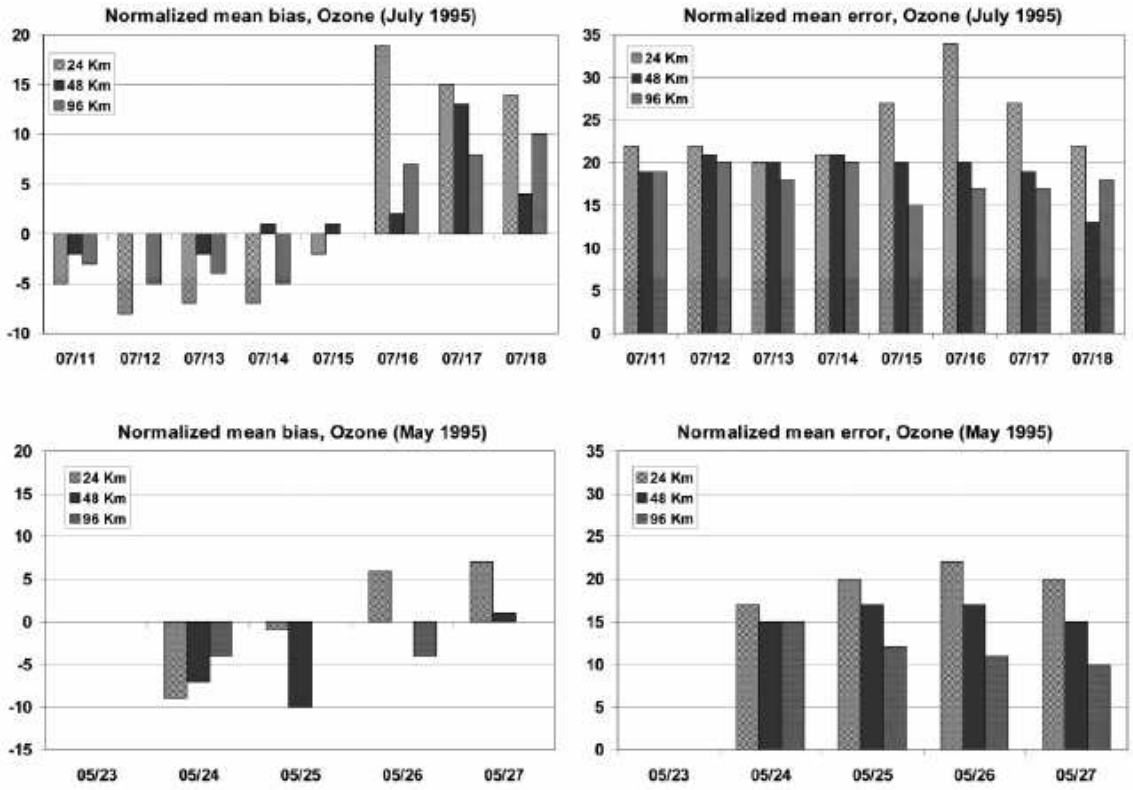


FIGURE 3. Ozone performance evaluation for the two basecase episodes and different grid resolutions.

and from 1-h or 8-h incremental reactivity values at the time of the maximum ozone concentration for each cell. While the MIR-3D and POIR-3D metrics are calculated from the values for a single cell and averaging period (but selected from all the cells/times), the LS-RR metric uses a larger number of cells/times that are of particular interest (high ozone concentration and/or significant base mixture reactivity).

Results and Discussion

Spatial distributions of ozone at the time of the peak are significantly different for the May and July basecase episodes (Figure 2). The May episode is considerably lower in ozone concentration and is characterized by lower temperatures and biogenic VOC emissions. Simulated ozone concentrations typically have acceptable bias compared to observations, and the normalized error is generally less than 25%

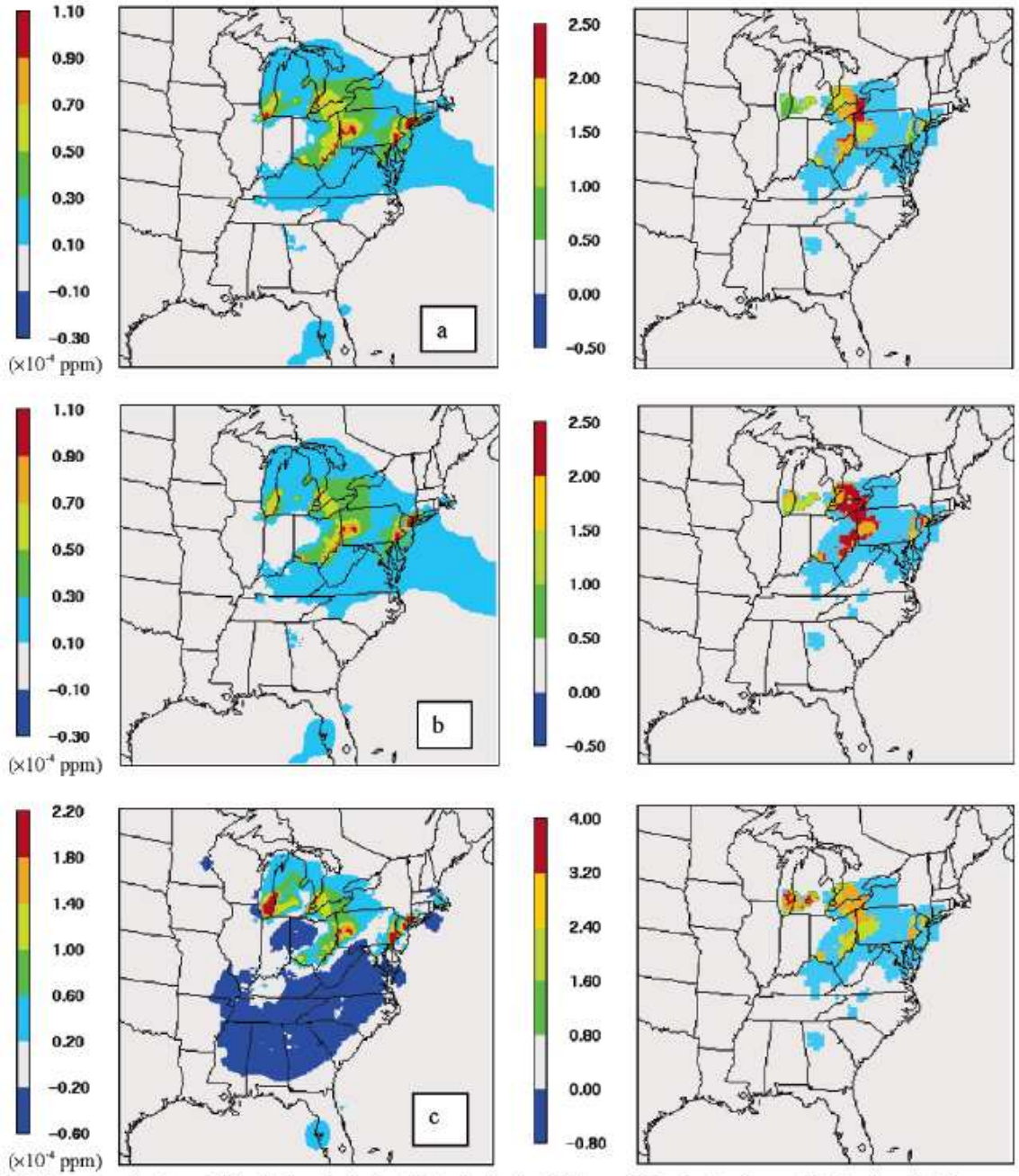


FIGURE 4. Sample of spatial distribution of absolute (left) and relative (right) reactivities for (a) *n*-butane, (b) ethanol, and (c) isoprene. Light blue in the relative reactivity plots represents areas with insignificant base mixture reactivity.

(Figure 3). Few observation sites with poor performance cause lower agreement in finer grid cells.

There is a large spatial and temporal variation in the absolute reactivities of VOCs, and less so in relative reactivities (Figures 4−6, July 1995 episode). Comparing time series for a VOC-limited urban air mass (Chicago) and NO_x-limited area dominated by biogenic emissions (Great Smoky Mountains, NC) shows an order of magnitude difference in species absolute reactivities (Figure 5). Time series for the relative reactivities in major urban areas (Figure 6) also show variability but at a much lower level than the absolute values. Rankings of organic species can change with time and location (e.g., formaldehyde and 2-methyl-2-butene), mainly in the case of absolute reactivities. Note that relative reactivities in Figures 4 and 6, at locations with base mixture reactivity less than 0.3 ppb, are not included in the calculations because the small denominator in eq 5 leads to large fluctuations in the relative reactivites. It is also for these locations, and during these periods that VOC controls have little impact on ozone concentrations, rendering reactivity-based strategies inefficient.

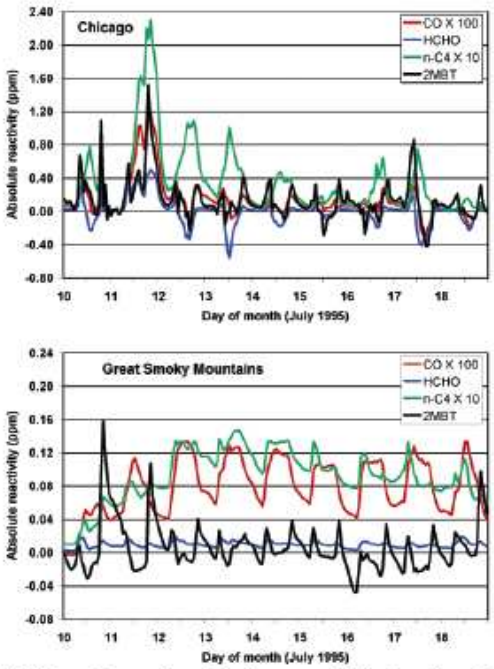


FIGURE 5. Time series of absolute reactivities for select VOCs at Chicago and Great Smoky Mountains, NC. See Table 4 for species codes.

Since the perturbation of emissions in the sensitivity field follows the pattern of the total VOC emissions, high VOC reactivities are found in areas (or downwind of areas) where anthropogenic emissions of both VOC and NO_x are highest. Organic reactivities, as expected, are considerably higher for VOC-limited air masses, where the peak ozone usually occurs (Figure 5). Among the four cities shown (Figure 6), only Chicago has significant negative base mixture reactivity at times, as it is the least radical-limited in the group.

Simulated species and their relative box model reactivity (relative MIR) (*25*) and the calculated 3-D reactivity metrics are given in Table 4. 1-h and 8-h least-squares metrics are calculated for an ozone concentration threshold of 60 ppb. As the July 1995 episode has significantly higher ozone concentrations, the 1-h threshold for that episode was set to 80 ppb. In least-squares calculations, the cells with negligible anthropogenic emissions and those with low base mixture reactivity (less than 0.1 ppb, about 1% of the maximum value for July 1995 episode) are excluded. Also, points with negative base mixture reactivity are excluded, as they can result in misleading metrics. Each calculated metric (for each species and episode) is the average of all the days that are available in that episode. A complete tabulation of both 1-h and 8-h metrics can be found in the Supporting Information.

Reactivity scales calculated from the 3-D model show good agreement with the box model values but cover a narrower range, i.e., they have lower reactivity for more reactive species than the box model (Figure 7). MIR-3D scales are closer to box model scales than the least-squares metric, as conditions in the maximum reactivity cell tend to be more similar to box model MIR conditions. Among all episodes, the MIR-3D metric of the July 1995 episode shows the worst agreement with the box model scales, as it has the highest (mainly biogenic) VOC emissions and is the least radical-limited. It is important to note that aldehydes are consistently lower in relative reactivity than the box model results. In addition to the less radical-limited condition, 3-D modeling also accounts

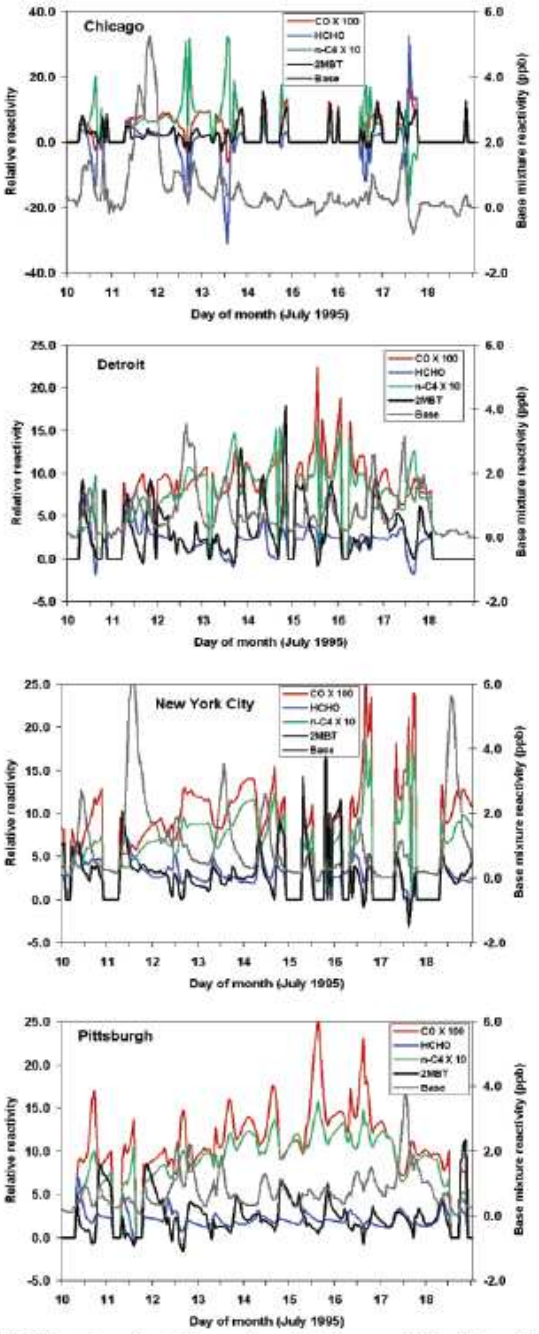


FIGURE 6. Samples of time series of relative reactivities (left axis) and the base mixture absolute reactivity (right axis) in 4 urban areas. Relative reactivities are calculated for the cells with base mixture reactivity greater than 0.3 ppb.

for the carryover of the species that provide a source for radicals (e.g. photolysis of ozone, nitrous acid, secondary carbonyls, hydrogen peroxide, etc.) into the next days. This sustained source of radicals makes the radical-producing organics less reactive than the box model simulation. Other significant differences between the box model scales include trimethylbenzene (although xylenes generally show good agreement) and α-pinene being higher in the box model,

TABLE 4: Summary of 1-h and 8-h MIR-3D and LS-RR Metrics[a]

		1-h									8-h								
		box model	July 1995		July 2010		May 1995		May 2010		box model	July 1995		July 2010		May 1995		May 2010	
compound	code	RMIR	MIR-3D	LS-RR	MIR-3D	LS-RR	MIR-3D	LS-RR	MIR-3D	LS-RR	RMIR	MIR-3D	LS-RR	MIR-3D	LS-RR	MIR-3D	LS-RR	MIR-3D	LS-RR
2-methyl-2-butene	2MBT	4.73	3.39	2.02	4.28	2.43	4.34	3.39	3.65	3.39	5.87	3.37	2.20	3.68	2.52	4.29	3.81	3.87	3.82
1,3-butadiene	BUTD	4.28	3.52	2.79	3.96	3.04	3.79	3.30	3.83	3.42	4.65	3.55	2.93	3.83	3.22	3.82	3.39	3.90	3.39
propene	PRPE	3.80	3.28	2.55	3.72	3.02	3.62	3.25	3.75	3.34	3.97	3.22	2.63	3.58	3.14	3.46	3.26	3.64	3.25
isoprene	ISOP	3.40	3.14	2.59	3.32	2.66	3.35	2.99	3.25	3.07	3.71	3.26	2.76	3.46	2.90	3.39	3.11	3.36	3.14
***m*-xylene**	XYLM	3.29	2.79	2.06	3.22	2.45	3.27	2.91	3.32	3.10	3.61	2.43	2.16	2.86	2.61	3.21	2.93	3.38	3.05
ethylene	ETHE	2.98	3.29	2.92	3.26	3.43	3.25	3.61	3.46	3.62	2.92	3.26	2.95	3.64	3.41	3.27	3.52	3.54	3.42
formaldehyde	HCHO	6.29	3.66	2.43	4.42	3.28	5.01	4.54	4.77	4.93	7.72	3.30	2.66	4.05	3.66	4.87	4.57	5.04	4.71
acrolein	ACRO	3.36	1.95	1.68	1.95	1.42	2.28	1.49	1.93	1.43	3.41	1.73	1.61	1.68	1.27	2.06	1.44	1.82	1.48
1,2,4-trimethylbenzene	124B	2.24	1.97	1.53	2.20	1.71	2.26	1.92	2.21	2.00	2.39	1.78	1.61	1.99	1.81	2.20	1.94	2.26	1.98
acetaldehyde	CCHO	3.52	2.23	1.90	2.18	1.74	2.67	1.78	2.45	1.80	3.74	2.05	1.88	2.11	1.60	2.39	1.73	2.04	1.75
a-pinene	APIN	1.37	1.15	0.90	1.18	0.84	1.43	1.06	1.17	1.03	1.53	1.14	0.95	1.10	0.93	1.35	1.17	1.16	1.16
***p*-xylene**	XYLP	1.32	1.31	1.20	1.37	1.30	1.32	1.31	1.39	1.34	1.27	1.23	1.23	1.33	1.33	1.31	1.29	1.40	1.30
toluene	TOLU	1.22	1.25	1.28	1.26	1.32	1.24	1.39	1.34	1.43	1.15	1.17	1.29	1.28	1.33	1.30	1.37	1.35	1.39
methylcyclopentane	MCPT	0.79	0.88	0.99	0.81	0.92	0.75	0.72	0.72	0.68	0.70	0.99	0.96	0.88	0.90	0.74	0.71	0.71	0.69
ethanol	ETOH	0.91	1.02	1.18	0.96	1.09	0.87	0.98	0.92	0.84	0.77	1.15	1.12	1.08	1.04	0.92	0.97	0.89	0.91
isopentane	IPNT	0.56	0.74	0.82	0.73	0.82	0.59	0.65	0.63	0.61	0.50	0.85	0.79	0.81	0.79	0.60	0.64	0.60	0.62
***n*-pentane**	N_C5	0.52	0.76	0.89	0.69	0.82	0.56	0.63	0.56	0.57	0.45	0.87	0.86	0.78	0.79	0.58	0.62	0.56	0.59
methyl ethyl ketone	MEK	0.62	0.56	0.63	0.54	0.56	0.58	0.55	0.55	0.51	0.58	0.61	0.60	0.57	0.53	0.59	0.54	0.54	0.53
2,2,4-trimethylpentane	224P	0.48	0.64	0.71	0.64	0.73	0.51	0.61	0.54	0.60	0.43	0.71	0.69	0.69	0.71	0.52	0.60	0.54	0.60
***n*-butane**	N_C4	0.45	0.60	0.71	0.57	0.65	0.45	0.51	0.47	0.45	0.39	0.70	0.68	0.63	0.62	0.46	0.50	0.45	0.47
acetylene	C2H2	0.38	0.39	0.41	0.41	0.43	0.36	0.46	0.41	0.45	0.33	0.39	0.39	0.41	0.41	0.39	0.46	0.41	0.46
***n*-butyl acetate**	BACT	0.40	0.57	0.67	0.53	0.60	0.44	0.47	0.47	0.42	0.35	0.66	0.65	0.58	0.58	0.46	0.47	0.44	0.43
benzene	C6H6	0.25	0.33	0.42	0.31	0.38	0.27	0.33	0.30	0.32	0.21	0.36	0.41	0.34	0.37	0.28	0.33	0.28	0.32
methyl *tert*-butyl ether	MTBE	0.32	0.50	0.56	0.49	0.56	0.40	0.47	0.44	0.45	0.29	0.57	0.54	0.55	0.55	0.41	0.46	0.41	0.45
methanol	MEOH	0.53	0.64	0.72	0.64	0.73	0.52	0.70	0.58	0.66	0.47	0.69	0.69	0.71	0.69	0.55	0.69	0.56	0.68
2-propanol	IPOH	0.33	0.50	0.47	0.52	0.54	0.43	0.47	0.46	0.45	0.32	0.54	0.47	0.57	0.53	0.44	0.47	0.47	0.45
dodecane	DODC	0.22	0.39	0.49	0.30	0.41	0.29	0.29	0.26	0.25	0.16	0.45	0.50	0.32	0.42	0.28	0.29	0.27	0.26
acetone	ACET	0.19	0.18	0.19	0.17	0.18	0.19	0.20	0.20	0.19	0.19	0.18	0.18	0.18	0.17	0.20	0.19	0.19	0.20
ethane	C2H6	0.11	0.14	0.18	0.13	0.15	0.10	0.11	0.10	0.09	0.09	0.17	0.17	0.15	0.14	0.10	0.11	0.09	0.10
carbon monoxide	CO	0.039	0.072	0.082	0.071	0.082	0.055	0.064	0.060	0.057	0.037	0.084	0.080	0.084	0.080	0.058	0.065	0.057	0.064
methane	CH4	0.004	0.007	0.008	0.007	0.008	0.005	0.006	0.006	0.006	0.007	0.008	0.008	0.008	0.007	0.005	0.006	0.005	0.006
higher aldehydes	RCHO	N/A	2.38	1.86	2.47	1.71	3.17	1.87	2.50	1.78	N/A	2.16	1.83	2.21	1.66	2.94	1.86	2.48	1.81
lumped alkanes	ALK3	N/A	0.64	0.76	0.62	0.72	0.48	0.58	0.52	0.53	N/A	0.75	0.73	0.71	0.69	0.51	0.57	0.50	0.55
lumped alkanes	ALK4	N/A	0.72	0.83	0.68	0.79	0.57	0.63	0.62	0.57	N/A	0.83	0.81	0.79	0.77	0.59	0.62	0.57	0.59
lumped alkanes	ALK5	N/A	0.78	0.90	0.68	0.81	0.64	0.64	0.63	0.58	N/A	0.88	0.89	0.74	0.81	0.62	0.63	0.60	0.58
lumped aromatics	ARO1	N/A	1.13	1.15	1.16	1.20	1.13	1.23	1.23	1.25	N/A	1.09	1.15	1.14	1.21	1.16	1.21	1.21	1.22
lumped aromatics	ARO2	N/A	2.29	1.77	2.45	2.01	2.54	2.32	2.79	2.46	N/A	2.03	1.88	2.39	2.13	2.58	2.34	2.64	2.42
lumped olefines	OLE1	N/A	2.68	2.25	2.71	2.42	2.90	2.51	2.95	2.50	N/A	2.66	2.34	2.87	2.54	2.80	2.52	2.82	2.47
lumped olefines	OLE2	N/A	2.36	1.80	2.45	1.79	2.76	2.16	2.53	2.09	N/A	2.36	1.91	2.46	1.92	2.67	2.32	2.46	2.28
lumped terpines	TRP1	N/A	1.06	0.88	1.14	0.83	1.19	0.97	1.00	0.93	N/A	1.20	0.93	1.08	0.92	1.19	1.07	1.07	1.05
benzaldehyde	BALD	−0.22	−0.47	0.11	−0.87	−0.32	−0.34	−0.27	−0.48	−0.11	−0.36	−0.77	0.14	−1.11	−0.30	−0.41	−0.29	−0.47	−0.12

[a] Box model (*25*) relative (per mole-C) reactivities are also shown. Explicit species that are added to the base mechanism are listed in bold.

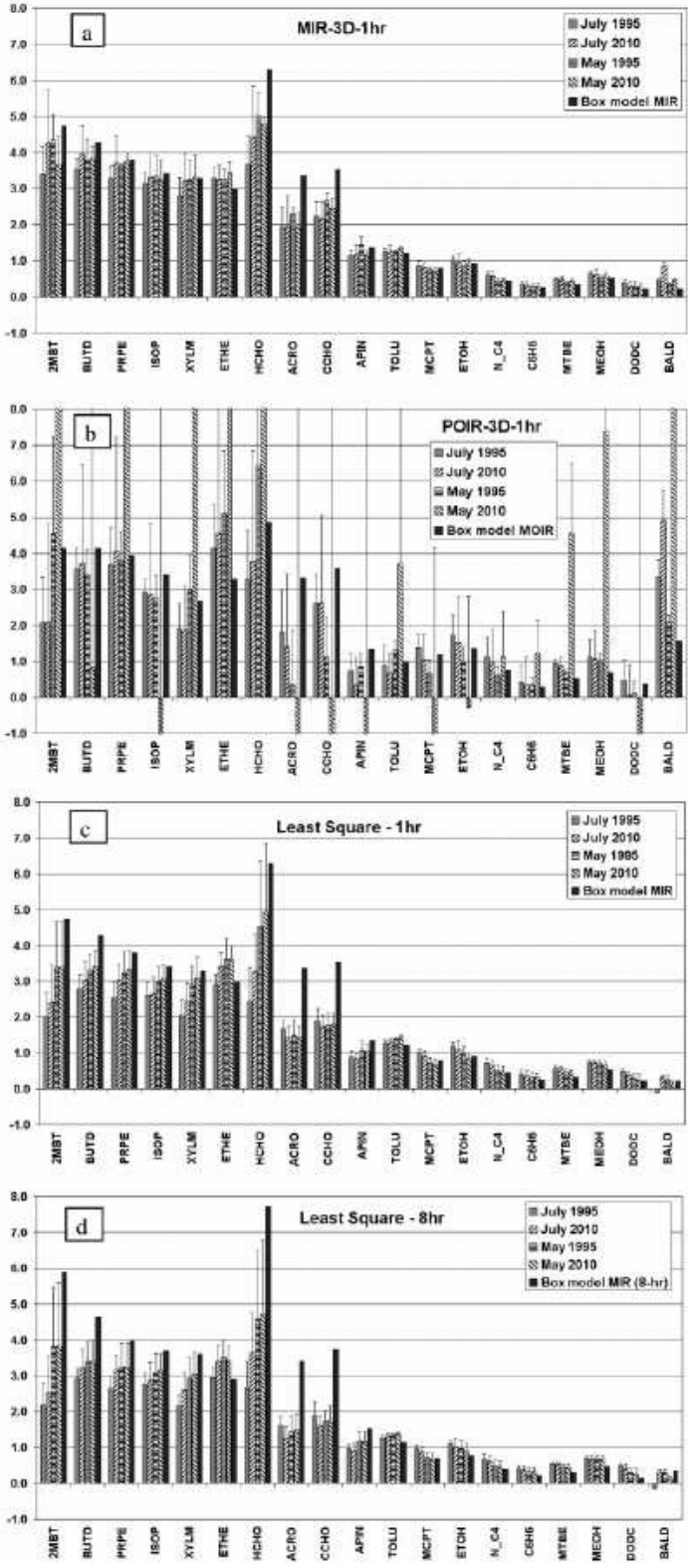


FIGURE 7. Comparison of different 3-D reactivity metrics for all episodes: (a) MIR-3D$_{1hr}$, (b) POIR-3D$_{1hr}$, (c) LS-RR$_{1hr}$, and (d) LS-RR$_{8hr}$.

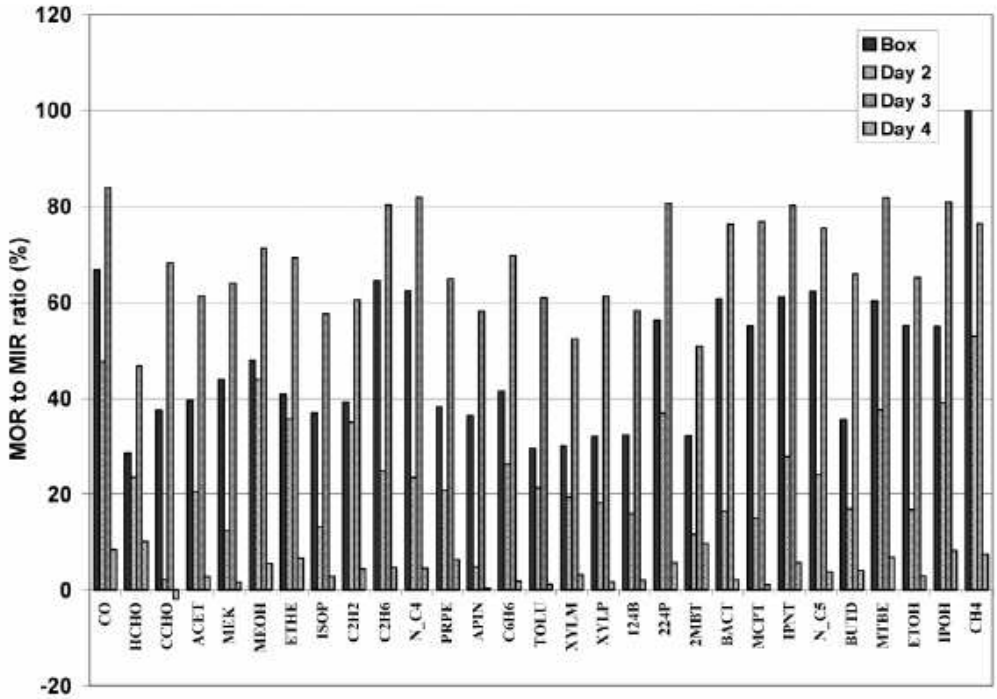


FIGURE 8. Comparison between ratio of maximum ozone reactivity and maximum reactivity for the box model and different days in 3-D modeling.

while methanol is somewhat lower (see the Supporting Information).

Given the significant temporal and spatial variability in absolute reactivities, the relative metrics are surprisingly comparable from one episode to another. Additionally, the relative ranking of species remains similar for different scales. As mentioned before, May episodes (1995 and 2010) have far less biogenics and are more radical-limited, resulting in higher reactivities for those more reactive VOCs that are important sources of radicals. Least-squares metrics generally show a high coefficient of determination and low standard error for the least-squares slope (relative reactivity) estimate (see the Supporting Information) with the exception of benzaldehyde. 1-h and 8-h scales are usually very similar in the ranking of the species (Figure 7c,d), and therefore, calculation of one averaging period seems to be sufficient for characterizing the behavior of organic compounds. POIR-3D scales are the most variable and inconsistent among different scales (e.g., Figure 7b) as the conditions at the location and time of the maximum ozone concentration can be significantly different than the box model. In Figure 8, the ratio of absolute reactivity at the peak ozone location and time to the maximum reactivity for each species is plotted in comparison to the box model ratio for the May 1995 episode. It can be seen that some of the days have similar behavior to the box model, while other days are significantly different. It can be concluded that POIR-3D is not a robust metric for comparing the ozone formation potential of organic compounds.

In a previous study, three-dimensional relative reactivity metrics were calculated for central California (*12*). For that study the same chemical mechanism (excluding explicit treatment of acrolein and dodecane) and methodology was applied for reactivity assessment, and, therefore, a comparison of the results is insightful for better understanding the effects of different domains on reactivity metrics. Figure 9a compares 1-h LS-RR reactivity scales for the July 1995 episode with those calculated for the episode/domain in California. Considering the significant differences in the chemical regimes in these two domains, the scales show good agreement. The slope is larger than one, mainly due to the highly reactive, radical producing VOCs being more reactive in the more radical-limited regime (central California, due to much lower biogenic emissions). In Figure 9b, a very good correlation between May and July 1995 episodes, for the LS-RR scale is seen. Slopes larger than one are expected, as May episodes are more radical-limited (lower biogenic emissions). Figure 9c also shows good correlation between reactivity scales in different emissions scenarios. Again, larger-than-one slopes (especially for least-squares metrics) show that with further emission control measures, the domain will become more sensitive to organic emissions, i.e., more radical-limited. Note that the least-squares metrics are driven by grid cells that have higher base mixture reactivity and tend to be downwind of urban areas. Such cells are mainly dominated by mobile and area source emissions and, therefore, are less affected by aggressive NO_x control from power plants in future years. The very high R^2 for the correlation between different emission scenarios (and identical meteorologies) suggests that the meteorology plays a significant role in defining the behavior of different reactivity metrics. Table 5 shows a summary of correlation and slopes for different pairs of reactivity scales or domains and episodes. In general, there is very good agreement with box model and three-dimensional scales for most species as well as between different 3-D scales.

All least-squares metrics presented so far are calculated using a two-parameter (slope and intercept) model. Forcing the least-squares line to pass through the origin (no-intercept model) will produce somewhat different results. The difference is small to modest for most species and episodes but can be significant for a few. A complete set of the least-squares points (grid cells and hours that are used for 1-h least-squares calculations) for all episodes and all species are presented elsewhere (Supporting Information). Both

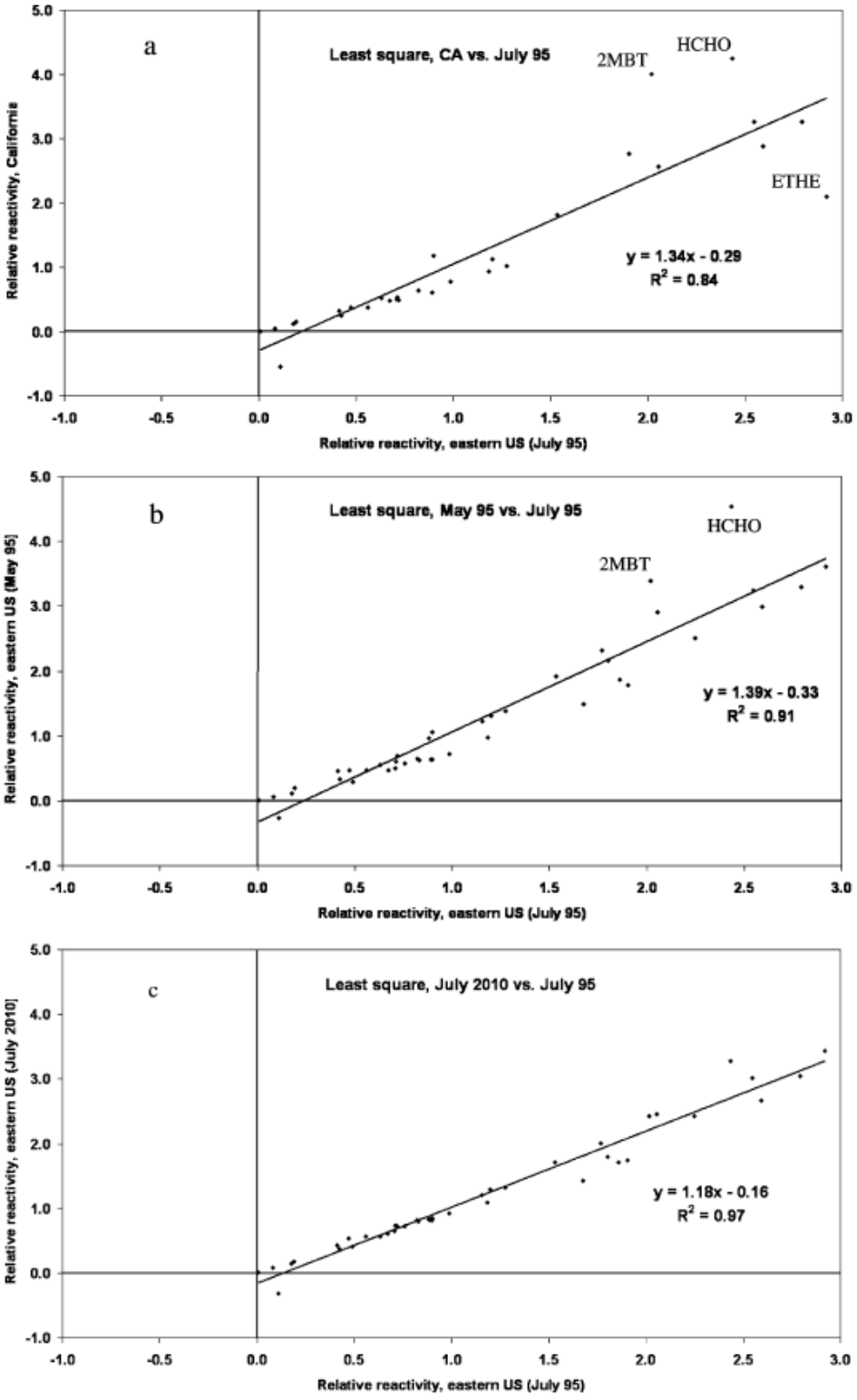


FIGURE 9. Comparison of 1-h LS-RR relative reactivity metrics between (a) different domains, (b) different episodes, and (c) different emission inventories.

TABLE 5: R-Squared (Top-Right Half) and Slope (Bottom-Left Half) for Correlation between Different (a) MIR-3D Metrics, (b) LS-RR Metrics with an Intercept Model, and (c) LS-RR Metrics with a No-Intercept Model[a]

a	July 1995	July 2010	May 1995	May 2010	CA	box model
July 1995		0.99	0.97	0.99	0.92	0.92
July 2010	1.15		0.98	0.98	0.95	0.94
May 1995	1.21	1.05		0.98	0.98	0.97
May 2010	1.16	1.00	0.95		0.95	0.95
CA	1.13	0.98	0.97	0.99		0.99
box model	1.21	1.05	1.01	1.04	1.03	

b	July 1995	July 2010	May 1995	May 2010	CA	box model
July 1995		0.97	0.91	0.89	0.84	0.81
July 2010	1.18		0.97	0.95	0.86	0.84
May 1995	1.39	1.20		1.00	0.92	0.91
May 2010	1.44	1.25	1.04		0.91	0.91
CA	1.34	1.13	0.95	0.90		0.98
box model	1.59	1.35	1.14	1.08	1.16	

c	July 1995	July 2010	May 1995	May 2010	CA	box model
July 1995		0.96	0.73	0.75	0.67	0.71
July 2010	1.25		0.77	0.87	0.67	0.70
May 1995	1.02	0.82		0.86	0.91	0.90
May 2010	1.29	1.09	1.16		0.72	0.67
CA	0.90	0.70	0.89	0.62		0.98
box model	1.32	1.03	1.06	0.77	1.16	

[a] Slopes are calculated for metrics in the vertical header with respect to the ones in the horizontal header.

intercept and no-intercept fits are shown for each species. Benzaldehyde is the species with very poor fit in both models. For some species a no-intercept model clearly provides a poor fit with low or even negative R^2 (*26*). In general, biogenics, lumped and substituted aromatics, most olefins, and acrolein tend to have a negative intercept, leading to a lower reactivity in the no intercept model. On the other hand, aliphatic hydrocarbons, alcohols, and MTBE usually have a positive intercept.

Results presented so far are calculated based on daily metrics. Calculating the least-squares relative reactivity from an episodic metric (all the points in the whole episode) can result in some differences. In addition to the magnitude of the relative reactivity fit, the coefficient of determination can be higher in one method or the other, depending on the daily characteristics of the episode. The May episodes tend to have more distinct daily characteristics than the July episodes. This is depicted in Figure 10, where the least-squares points (for 5 days in July and all days in May) for formaldehyde are shown separately for each day. A daily distinction can be seen for both May episodes. This results in higher R^2 for the daily approach, while for the July episode such distinction does not exist, and therefore the R^2 for the episodic metric is higher (as some days with fewer points can have much lower R^2).

As shown, applying direct sensitivity analysis to air quality models proves to be an efficient method for comprehensive reactivity analysis. 3-D reactivity assessment shows that reactivity scales are generally robust over different environmental conditions and domains. Future control strategies are not likely to significantly change the relative reactivities of the organics. However, this assessment also reveals important differences between the box model and 3-D results, e.g., carbonyl reactivity, or scales based on maximum ozone concentrations (MOIR and POIR). MIR-3D scales show the best agreement with the box model MIR, but they represent regimes with the greatest effectiveness for VOC control. Least-squares metrics are representative of a wider range of

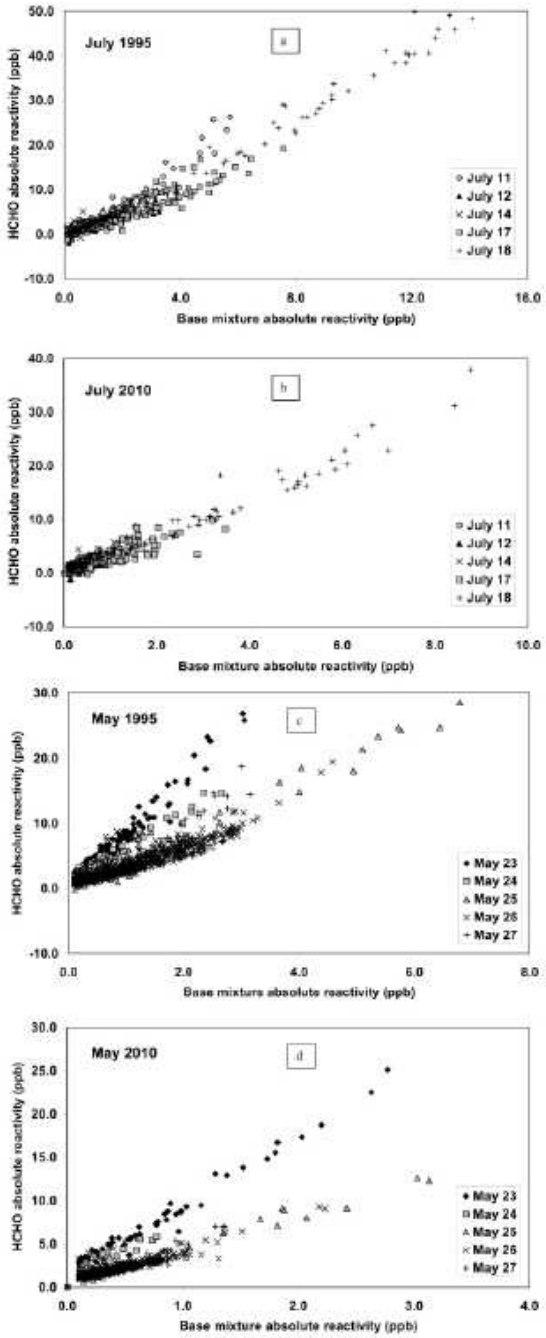


FIGURE 10. The grid cells and hours used in the calculation of 1-h least-squares metrics for (a) July 1995, (b) July 2010, (c) May 1995, and (d) May 2010.

environmental/chemical conditions, but they exhibit somewhat greater daily, episodic, and spatial variability. Taking these complexities into account is crucial in devising effective VOC-based regulations or control strategies.

Acknowledgments

This work was supported by the American Chemistry Council and the California Air Resources Board and by funding from U.S. EPA under contracts RD-83096001 and RD-82897601.

The authors are grateful to Dr. William Carter for his kind help, in particular with base mixture composition and least-squares metric definition. We also thank Dr. Jana Milford for providing the SAPRC-99 mechanism used in this study. The spatial plots in this paper are produced using PAVE by MCNC.

Supporting Information Available

1-h and 8-h relative MIR-3D and MOIR-3D reactivity metrics (Tables S1−S4), 1-h and 8-h relative LS-RR reactivity metrics (Tables S5−S12), and least-squares metrics (1-h) for intercept and no-intercept models (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Russell, A. G.; Milford, J.; Bergin, M. S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W. R.; Croes, B. *Science* **1995**, *269*, 491−495.
(2) Bergin, M. S.; Russell, A. G.; Milford, J. B. *Environ. Sci. Technol.* **1995**, *29*, 3029−3037.
(3) CARB. *Proposed Regulations for Low-Emission Vehicles and Clean Fuels- - Staff Report and Technical Support Document*; California Air Resources Board: Sacramento, CA, August, 1990.
(4) CARB. *Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'*; California Air Resources Board: Sacramento, CA, May, 2000.
(5) Carter, W. P. L. *J. Air Waste Manage. Assoc.* **1994**, *44*, 881−899.
(6) Carter, W. P. L. *Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment*; Draft report to the California Air Resources Board; Contracts 92-329 and 95-308; Riverside, CA, 2000a.
(7) McNair, L.; Odman, M. T.; Russell, A. G. *J. Air Waste Manage. Assoc.* **1992**, *42*, 174−178.
(8) Khan, M.; Yang, Y.-J.; Russell, A. G. *Atmos. Environ.* **1999**, *33*, 1085−1092.
(9) Carter, W. P. L.; Tonnesen, G.; Yarwood, G. *Investigation of VOC Reactivity Effects Using Existing Regional Air Quality Models*; Final report to American Chemistry Council, Contract SC-20.0-UCR-VOC-RRWG; April, 2003. http://www.cert.ucr.edu/~carter/absts.htm#ddmrep+1.
(10) Martien, P.; Harley, R. A.; Milford, J. B.; Russell, A. G. *Environ. Sci. Technol.* **2003**, *37*, 1598−1608.
(11) CARB. *Development of Reactivity Scales via 3-D Grid Modeling of California Episodes;* Final Report, contract No. 98-309; 2002.
(12) Hakami, A.; Harley, R. A.; Milford, J. B.; Odman, M. T.; Russell, A. G. *Atmos. Environ.* **2004**, *38*, 121−134.
(13) Yang, Y.-J.; Wilkinson, J. G.; Russell, A. G. *Environ. Sci. Technol.* **1997**, *31*, 2859−2868.
(14) RSAC. *Minutes of the Reactivity Scientific Advisory Committee meeting on October 8, 1999.* http://www.arb.ca.gov/research/reactivity/rsac/oct99-min.html, accessed March 2003.
(15) Kumar, N.; Odman, M. T.; Russell, A. G. *J. Geophys. Res.* **1994**, *99*, 5385−5398.
(16) Boylan, J. W.; Odman, M. T.; Wilkinson, J. W.; Russell, A. G.; Doty, K.; Norris, W.; McNider R. *Atmos. Environ.* **2002**, *36*, 3721−3734
(17) Bergin, M. S.; Shih, J.-S.; Boylan, J. W.; Wilkinson, J. G.; Krupnick, A.; Russell, A. G. *Inter- and Intra-State Impacts of NO_x and SO_2 Emmisions on Ozone and Fine Particulate Matter; 2004, In preparation.*
(18) Young, T. R.; Boris, J. P. *J. Phys. Chem.* **1977**, *81*, 2424−2427.
(19) Colella, P.; Woodward, P. R. *J. Copm. Phys.* **1984**, *54*, 174−201.
(20) Odman, M. T.; Boylan, J. W.; Wilkinson, J. G.; Russell, A. G.; Doty, K.; Norris, W.; McNider, R.; Mueller S. F.; Imhoff R. E. *SAMI Air Quality Modeling Final report*; Southern Appalachian Mountains Initiative: Asheville, North Carolina, 2002; 205 pp.
(21) McRae, G. J.; Goodin, W. R.; Seinfeld, J. H. *Atmos. Environ.* **1982**, *16*, 679−696.
(22) Dunker, A. M. *Atmos. Environ.* **1981**, *15*, 1155−1161.
(23) Dunker, A. M. *J. Chem. Phys.* **1984**, *81*, 2385−2393.
(24) Carter, W. P. L. 2002 personal communication.
(25) Carter, W. P. L. VOC reactivity data as of November 13, 2000, 2000b. ftp.cert.ucr.edu/pub/carter/SAPRC99/r99tab.xls. Accessed March, 2001.
(26) Kvalseth, T. O. *Am. Statistician* **1985**, *39*, 279−285.

Received for review December 30, 2003. Revised manuscript received August 5, 2004. Accepted August 17, 2004.

ES035471A